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HUMIC SUBSTANCES IN NATURAL WATERS AND THEIR COMPLEXATION WITH TRACE METALS AND RADIONUCLIDES: A REVIEW

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ABSTRACT

Dissolved humic substances (humic and fulvic acids) occur in surface waters and groundwaters in concentrations ranging from less than 1 mg(C)/L to more than 100 mg(C)/L. Humic substances are strong complexing agents for many trace metals in the environment and are also capable of forming stable soluble complexes or chelates with radionuclides. Concentrations of humic materials as low as 1 mg(C)/L can produce a detectable increase in the mobility of some actinide elements by forming soluble complexes that inhibit sorption of the radionuclides onto rock materials. The stability of trace metal- or radionuclide-organic complexes is commonly measured by an empirically determined conditional stability constant (K'), which is based on the ratio of complexed metal (radionuclide) in solution to the product concentration of uncomplexed metal and humic complexant. Larger values of stability constants indicate greater complex stability.

The stability of radionuclide-organic complexes is affected both by concentration variables and environmental factors. In general, complexing is favored by increased concentration of humic or fulvic acid, decreased concentration of radionuclide, increased pH, and decreased ionic strength. Actinide elements are generally most soluble in their higher oxidation states. The presence of high concentrations of humic substances tends to reduce actinides to their less soluble state; however, competitive chelation by the humic substances acts in the opposite direction to increase solubility.

Radionuclides can also form stable, insoluble complexes with humic materials that tend to reduce radionuclide mobility. These insoluble complexes may be radionuclide-humate colloids that subsequently precipitate from solution, or complexes of radionuclides and humic substances that sorb to clay minerals or other soil particulates strongly enough to immobilize the radionuclides. Colloid formation appears to be favored by increased radionuclide concentration and lowered pH; however, the conditions that favor formation of insoluble complexes that sorb to particulates are still poorly understood.

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I. INTRODUCTION

High molecular weight compounds of humic and fulvic acids occur in small concentrations in natural surface waters and groundwaters. These humic substances are the major organic constituents of soils and sediments. They are described, generally, as polymers with molecular weights from 300 to 30,000. The humic substances form through the breakdown of plant and animal tissues by chemical and biological processes that tend to produce complex chemical structures that are more stable than the original material from which they were derived [SCHNITZER-1978]. One of the more important characteristics of humic substances is their ability to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides and to interact with clay minerals and various organic compounds such as alkanes, fatty acids, and toxic organic substances such as pesticides. The characteristics of natural humic materials, their origin, and their complexes with naturally present metals have recently been reviewed [BOGGS-1985].

The formation of water-soluble complexes of humic substances with metal ions is of particular interest because complexing can increase concentrations of these ions in natural waters far above the concentrations that could be expected based on the solubilities of inorganic species. The metals may be transported in flowing groundwaters, followed by destruction of the metal-humic substance bond at elevated temperature, and this is thought to give rise to the formation of ore deposits. In any case, the solubilities of simple ore minerals have long been recognized to be inadequate to form some ores [BARNES]. Apparently aqueous complexes are responsible for forming these ores, with organic humic and fulvic acids being one group of ligands important in the formation of some ores [SAXBY]. Many low-temperature deposits of sulfide minerals have associated organic solids and aqueous species. However, little has been done to date to characterize these materials. Responsible scientists must be concerned about the possibility that complexing of disposed metal-containing wastes by humic substances may enhance the mobility of these metals and promote their entry into the biosphere. This potential problem has special pertinence to the siting of radioactive waste repositories where the complexed metals may be radioactive. Therefore, for a better understanding of both the occurrence of our natural resources and the possible dispersion of disposed waste, it is important that we develop a fuller understanding of the ability of dissolved humic substances to form complexes with dangerous metals. We may then be able to assess our natural mineral resources more accurately and to take adequate precautions to prevent the dispersal of disposed radionuclides.

Section II presents the origin and characteristics of humic materials as we understand them today and outlines the methods that have been used to separate and analyze these substances.

Section III focuses on the general problem of metal-organic interactions and treats some of the factors that are important in chelating and complexing of metal ions by humic substances.

Section IV deals specifically with the complexing of radionuclides by organic substances, treated from the standpoint of both empirical and experimental studies.

Because the complexing of radionuclides by organic substances is the subject of our ongoing work, we attempted to be comprehensive in the final part of the review by considering all recent relevant publications. They were identified from computer-stored and -retrieved data files. In addition, subject and author indexes of major chemical and geochemical journals were searched for relevant publications. Finally, indexes of citations to major works in this subject were examined to reveal relevant publications that were missed in the other searches. As a result of this effort, we feel we have identified a reasonably comprehensive list of publications (several hundred) for developing the review, and many of these publications have been cited herein.

II. DISTRIBUTION AND CHARACTERIZATION OF DISSOLVED HUMIC SUBSTANCES IN NATURAL WATERS

A. Dissolved Organic Carbon Content of Natural Waters

Most natural waters contain some dissolved organic carbon (DOC); however, surprisingly few measurements of the organic carbon content of natural waters have been made. This scarcity of data is apparently because most scientists have been primarily concerned with the inorganic composition of natural waters and, until recently, have had little interest in the dissolved organic constituents. The lack of a simple, inexpensive method for determining the organic carbon content of waters, particularly those with low DOC levels, has probably also hampered collection of DOC data.

Stumm and Morgan [STUMM] suggest that concentrations of DOC in natural waters range from about 0.1 mg/L in seawater and some unpolluted and nonproductive fresh waters to 10 mg/L in lakes, streams, and estuaries; however, the value of 10 mg/L is clearly too low as an upper range for DOC concentrations in lakes and streams because much higher values have been reported. For example, Malcolm and Durum [MALCOLM] report an average value of 27 mg/L DOC in the Sopchoppy River in Florida, and Thurman [THURMAN-1979] reports 32 mg/L in the Suwannee River of Georgia. Reuter and Perdue [REUTER-1977] indicate that rivers draining the coastal plains of the southeastern United States in regions of abundant swamps contain concentrations of humic substances as high as 100 mg(C)/L with a mean value of about 45 mg(C)/L; however, these values may also include particulate carbon (>0.45 μm). Thus the DOC content of these waters is probably lower than the total organic carbon (TOC) content reported. (Most investigators arbitrarily place the particle size boundary between "dissolved" organic carbon and particulate organic carbon at 0.45 μm. Thus, all organic carbon that passes through a 0.45-μm filter is considered DOC). Christman and Gjessing [CHRISTMAN-1983B] point out that DOC values in streams vary considerably with climatic zones, ranging from 3 mg/L in temperate and arid zones to 6 mg/L in tropical zones and 10 mg/L in subarctic zones. Meybeck [MEYBECK] reported a stream volume weighted world average of 5.75 mg(DOC)/L. Values of DOC as high as 115 mg/L have been found in some high pH, alkaline lakes [WAHLGREN-1982].

Ocean water appears to have a lower DOC content than most lakes and streams. Williams [WILLIAMS] reports that the average concentration of DOC in the oceans from depths of 0-300 m is 1.0 mg/L and from 300-3800 m is 0.5 mg/L; however, values as high as 3 mg/L have been found in some parts of the Gulf of Mexico [HARVEY].

Published data on the DOC content of groundwaters are sparse. Means [MEANS-1982A] reports the DOC values of waters from nine deep wells in granitic and basaltic rocks in Washington and Sweden range from less than 1 mg/L to as much as 20 mg/L. Leenheer and Bagby [LEENHEER-1982] sampled waters from 77 wells (at depths ranging to 210 m) from basaltic and volcanic rocks and interbedded sediments at the Idaho National Engineering Laboratory and measured DOC values ranging from 1.6 to 18.0 mg/L (average, 6.1 mg/L). Values of DOC as high as 18 to 20 mg/L are not typical, however, and most groundwaters appear to contain only a few mg/L DOC. In fact, Leenheer et al. [LEENHEER-1974] found that the mean DOC concentration of 100 groundwaters

in sandstones, limestones, and crystalline rocks from various locations (10-400 m deep) was 1.2 mg/L. Grigoropoulos and Smith [GRIGOROPOULOS] measured the organic carbon content of 13 wells and springs in Missouri and found that the DOC content ranged from 0.003 to 0.3 mg/L in springs and from 1.0 to 5.5 mg/L in shallow groundwaters. Robinson et al. [ROBINSON] examined the organic carbon in groundwaters from five small towns in Illinois and reported DOC values ranging from 1.5 to 7.2 mg/L. Thurman [THURMAN-1979] measured the DOC in the groundwaters of five aquifers from various parts of the United States and obtained values ranging from 0.2 to 13 mg/L.

Much higher values of DOC are found in some deep formation waters (many of which are brines) associated with oil and gas fields. Carothers and Kharaka [CAROTHERS] found concentrations of organic acids (mainly short-chain fatty acids ranging from acetic acid to butric acid) in formation waters in California and Texas that ranged from 50 mg(C)/L for low temperature waters (less than about 80°C) to 4900 mg(C)/L for higher temperature waters (80-200°C). Means [MEANS-1982B] reports values of 12.8 to 76.5 mg/L DOC in formation waters from deep wells in some petroleum-producing basins such as the Paradox Basin in Utah and the Permian Basin of New Mexico and Texas.

B.   Types of Organic Carbon Compounds

The dissolved organic substances in natural waters encompass a wide range of compounds from CH_4 to high molecular weight polymers, and include functional groups* ranging from hydrocarbons to complex multifunctional compounds [FAULKNER]. These organic compounds are derived by biological and biochemical degradation of organic life substances. Table 1 shows a greatly simplified list of these substances that have been reported in natural waters. Note that the organic decomposition products include both humic substances (humic and fulvic acids) and large numbers of non-humic substances such as amino acids, fatty acids, phenols, sterols, natural sugars, hydrocarbons, urea, and porphyrins. Many organic compounds in natural waters are complex polymers that consist of large molecules made up of many repeating subunits (monomers). If these polymeric organic substances contain a sufficient number of polar or hydrophilic functional groups such as $-COO^-$, $-NH_2$, R_2NH, $-RS^-$, ROH, and RO^-, they will remain in solution despite their large molecular size [STUMM]. These large polymers include polypeptides, certain lipids, polysaccharides, and humic substances.

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*The term "functional group" refers to the molecules of compounds in a particular family of organic compounds such as alkanes, alcohols, or esters that are characterized by the presence of a certain arrangement of atoms; e.g., the -COOH carboxyl functional group. The functional group is that part of the molecule where most of its chemical reactions occur and is the part that effectively determines the compound's chemical properties. The properties of a functional group are very similar whether it appears in a simple compound or a complex molecule.

Table 1. **Naturally Occurring Organic Substances.**[a] Copyright 1981 John Wiley & Sons. Reprinted by permission [STUMM].

Life Substances	Decomposition Intermediates	Intermediates and Products Typically Found in Nonpolluted Natural Waters
Proteins	Polypeptides → RCH(NH$_2$)COOH → $\begin{cases} RCOOH \\ RCH_2OHCOOH \\ RCH_2OH \\ RCH_3 \\ RCH_2NH_2 \end{cases}$ amino acids	NH$_4^+$, CO$_2$, HS$^-$, CH$_4$, HPO$_4^{2-}$, peptides, amino acids, urea, phenols, indole, fatty acids, mercaptans
Polynucleotides	Nucleotides → purine and pyrimidine bases	
Lipids Fats ⎫ Waxes ⎬ Oils ⎭ Hydrocarbons	RCH$_2$CH$_2$COOH + CH$_2$OHCHOHCH$_2$OH → $\begin{cases} RCH_2OH \\ RCOOH \\ \text{shorter chain acids} \\ RCH_3 \\ RH \end{cases}$ fatty acids glycerol	CO$_2$, CH$_4$, aliphatic acids, acetic, lactic, citric, glycolic, malic, palmitic, stearic, oleic acids, carbohydrates, hydrocarbons
Carbohydrates Cellulose ⎫ Starch ⎬ Hemicellulose ⎭	C$_x$(H$_2$O)$_y$ → $\begin{cases} \text{monosaccharides} \\ \text{oligosaccharides} \\ \text{chitin} \end{cases}$ → $\begin{cases} \text{hexoses} \\ \text{pentoses} \\ \text{glucosamine} \end{cases}$	HPO$_4^{2-}$, CO$_2$, CH$_4$, glucose, fructose, galactose, arabinose, ribose, xylose
Lignin	(C$_2$H$_2$O)$_x$ → unsaturated aromatic alcohols → polyhydroxy carboxylic acids	
Porphyrins and Plant Pigments Chlorophyll ⎫ Hemin ⎬ Carotenes and ⎬ Xantophylls ⎭	Chlorin → pheophytin → hydrocarbons	Phytane Pristane, carotenoids Isoprenoid, alcohols, ketones, acids Porphyrins
Complex Substances Formed from Breakdown Intermediates, e.g.,	Phenols + quinones + amino compounds → Amino compounds + breakdown products of carbohydrates →	Melanins, melanoidin, gelbstoffe Humic acids, fulvic acids, "tannic" substances

[a] R is the symbol used to represent any alkyl group [CH$_3^-$(methyl); CH$_3$CH$_2^-$(ethyl); CH$_3$CH$_2$CH$_2^-$(propyl); CH$_3$CHCH$_3$(isopropyl)].

The organic fractions of groundwaters are found associated with inorganic anion and cation fractions of groundwaters that can be fractionated by filtration. Using filters characterized as allowing molecules smaller than 1000 molecular weight to pass (1000 mol wt cutoff filters), Boggs et al. [BOGGS-1984B] found that about 20% of the Mg, Ca, Sr, and Ba and much of the sulfate (~80%) in groundwaters from basaltic rock remained associated with the water fractions enriched in organic molecules v ...ation. These results suggest that complexes of inorganic-organic molecules can constitute a substantial fraction of the total amount of some elements in groundwaters.

Humic substances make up a high percentage of the total DOC in natural waters, and appear to be the single most abundant organic constituents of these waters; however, wide variations in the humic content of natural waters appear to exist. Reuter and Perdue [REUTER-1977] report that, on the average, humic materials constitute 60 to 80% of the total DOC in surface waters. Christman and Gjessing [CHRISTMAN-1983A] discuss data indicating that 48% of the organic carbon in North Carolina terrestrial waters is humic/fulvic material. Thurman, in Christman and Gjessing [CHRISTMAN-1983A], suggests that about 10% of the DOC in streams consists of identifiable compounds such as amino acids, carbohydrates, and volatile fatty acids. The balance consists of carbon in polymeric form (90% of DOC), about 50% of which is humic in nature. Harvey et al. [HARVEY] report that humic and fulvic acids make up 50 to 98% of the DOC in Mississippi River outflow water and from 10 to 50% in other parts of the Gulf of Mexico. Few data are available on the relative fraction of the total DOC in groundwaters that consists of humic substances. Thurman [THURMAN-1979] examined groundwaters from five aquifers in various areas in the United States and determined that humic substances make up from 5 to 33% of the total DOC in four of the aquifers and 66% in the remaining aquifer. He concluded from his data that groundwaters are depleted in humic substances relative to surface waters.

Humic substances are also the major organic constituents of soils and sediments. They are widely distributed over the earth's surface in both terrestrial and aquatic environments, and they have received far more study than other species of dissolved organic compounds. They also appear to be the most important type of organic compounds with respect to their ability to form stable complexes with metal ions. Because of their potential for complexing radionuclides and their abundance in some natural waters, humic substances are of great interest and concern in the disposal of radioactive wastes. The remainder of this report is devoted to discussion of the characteristics of these humic substances and their interactions with metal ions and radionuclides.

C.   General Characteristics of Humic Substances

Humic substances differ from other organic substances found in soils and natural waters because they no longer possess the specific physical and chemical properties that characterize well-defined organic compounds. They are dark-colored, acidic, predominantly aromatic [containing one or more benzene rings (C_6H_6)], hydrophilic (polar molecules with an affinity for water), chemically complex, polyelectrolyte-like materials that range in molecular weight from a few hundred to several thousand [SCHNITZER-1978]. Stumm and

Morgan [STUMM] describe humic substances as polymers (300 to 30,000 mol wt) containing phenolic OH and carboxylic groups with a lower number of aliphatic OH groups.*

Humic substances are commonly divided into three fractions based on their solubility in acid and alkaline solutions: (1) humic acid, which is soluble in alkaline solutions but is precipitated by acidification; (2) fulvic acid, which is the humic fraction that remains in the aqueous acidified solutions and is soluble in both acid and base; and (3) humin, the insoluble humic fraction of soils that cannot be extracted by either acid or base.

Although the chemical structure of humic substances is not well known, the three humic fractions are believed to be structurally similar. Fulvic acid appears in general to have a lower molecular weight than humic acid, but with more hydrophilic functional groups than humic acid or humin [SCHNITZER-1972]. In a study of fulvic and humic acid fractions extracted from marine clays, Rashid and King [RASHID-1969 -1971] found that the molecular weight of fulvic acid ranges from less than 700 to 10,000, with about 32% by weight of the fulvic acid in the molecular weight group less than 700, 20% from 700 to 5000, and 47% from 5000 to 10,000. Humic acid fractions showed a much wider range of values, extending from less than 700 to more than 2,000,000. Ishiwatari [ISHIWATARI] reported similar ranges of molecular weights; however, Schnitzer and Khan [SCHNITZER-1978] suggest that some of these molecular weights may be excessively high.

D.   Chemical Composition and Structure of Humic Substances

   1.   Elemental Composition

       Humic substances are composed predominantly of carbon, oxygen, hydrogen, and nitrogen, and contain small amounts of sulfur. Table 2 shows that the carbon composition of humic acids derived from selected soils ranges from about 51 to 62%. The carbon composition of fulvic acids is somewhat lower, ranging from 43 to 47%. Oxygen levels are correspondingly lower in humic acid (31 to 36%) than in fulvic acid (45 to 49%). In general, soil humic acids contain about 10% more carbon and 10% less oxygen than fulvic acids. Humic substances in soils also contain about 1 to 7% nitrogen and 0.1 to 1.5% sulfur (not shown in Table 2). Plechanov et al. [PLECHANOV] investigated the elemental composition of several river waters (Table 3). They report carbon values ranging from 53 to 56% for humic acid and 41 to 53% for fulvic acid. These data suggest that humic acids in rivers may be slightly depleted in carbon relative to soils. Gjessing [GJESSING] also found that humic substances in surface waters contain somewhat less carbon and nitrogen than soil humic compounds; however, Thurman [THURMAN-1979] observed that the carbon levels in the groundwaters of five selected aquifers were richer in carbon than soil humic substances (Table 4) but were generally somewhat depleted in oxygen and nitrogen.

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*Phenols are compounds that have a hydroxyl (OH) group attached directly to an aromatic ring; i.e., a benzene ring. Carboxyl groups contain the univalent organic radical (-COOH). Aliphatic groups are straight or branched, open-chain hydrocarbons having the empirical formula C_nH_{2n+2}; e.g., alkanes, alkenes, and alkynes.

Table 2. Elemental Composition of Humic Acids (HA) and Fulvic Acids (FA) Extracted by Alkali from Different Soils and Materials. Copyright 1978 John Wiley & Sons. Reprinted by permission [HAYES].

Sample	% C		% O		% H		% N	
	HA	FA	HA	FA	HA	FA	HA	FA
Sod podzolic	57.6	42.6	35.3	44.6	5.2	5.0	4.8	4.1
Chernozem	62.1	44.8	31.4	49.4	2.9	3.4	3.6	2.3
Inceptisol (surface)	54.5	42.8	34.1	47.7	5.3	3.8	5.5	2.0
Inceptisol (subsurface)	51.4	46.9	36.0	44.6	6.7	4.5	4.9	2.3
Brown coal	63.1		(32.7)[a]		2.8		1.4	
Brown coal[b]	65.4				4.0			
S. chartarum	57.3		27.7		7.0		6.8	
S. atra	53.1		34.8		5.7		5.4	

[a]The parenthetical entry was determined by subtracting the weights of the other constituents from 100%.

[b]Second source.

2. Oxygen-Containing Functional Groups

Hayes and Swift [HAYES] suggest that carboxyl, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, and possibly quinone and methoxyl groups are the principal functional groups in humic substances. Ether, ester, and ketone groups may also be present (Table 5). The means of ranges in acidity of selected functional groups (in meq/g) are given in Table 6. Total acidity in Table 6 refers to the sum of the CO_2H + phenolic OH groups. Note that the total acidity and especially the CO_2H content of fulvic acids are considerably higher than those of humic acids. Both contain about the same concentrations of phenolic OH, C=O, and OCH_3 groups per unit weight, but the fulvic acids are richer in alcoholic OH groups [SCHNITZER-1978].

3. Chemical Structure

The chemical structure of humic substances is still incompletely known; however, new analytical advances hold hope for eventually character-izing the structure of humic substances. Most of our knowledge of the chemical structure of humic materials comes from degradative studies in which the more complex humic substances are broken down into simpler substances that can be characterized. Degradation products of humic and fulvic acids are mainly phenolic and benzene carboxylic acids; however, owing to the degradative methods used in isolating these compounds, it is not known if they could have originated from more complex aromatic structures or could have occurred in the initial humic material in essentially the same forms in which they were isolated but held together by relatively weak bonding [SCHNITZER-1978].

Table 3. Elemental and Functional Group Analyses of Humic Acids and Fulvic Acids.[a] [PLECHANOV].

Sample	% C	% H	% N	% O	% S	% Ash	%-OCH3	-COOH (meqv/g)[b]
FA-0	51.96	4.32	1.04	39.80	3.05	<0.02	6.5	4.25
FA-1	53.32	4.51	1.20	38.90	1.77	0.03	8.2	4.00
HA-1	56.00	4.51	1.36	37.25	0.72	0.37	6.0	4.25
FA-2	53.15	4.76	1.04	37.59	2.60	1.02	7.7	3.95
HA-2	55.29	4.53	1.26	37.08	1.78	0.25	6.1	4.15
FA-3	51.47	4.51	1.63	40.78	1.14	0.34	1.9	3.80
HA-3	55.00	4.30	2.10	n.d.[c]	0.8	n.d.	n.d.	3.33
FA-RT[d]	41.4	5.1	2.8	49.5	n.d.	1.18	n.d.	4.31
FA-OR[e]	51.1	3.62	1.13	n.d.	n.d.	1.0	n.d.	6.8
HA-OR[e]	53.4	3.73	2.10	n.d.	n.d.	4.3	n.d.	4.5

[a]Elemental, ash, and methoxyl analyses were carried out by Prof. Dipl. Ing., Dr. H. Malissa, G. Reuter Analytische Laboratorien, Elbach (Germany) and by the Analytical Laboratory, Studsvik Energiteknik AB (Sweden).

[b]Determined in this work by potentiometric titration.

[c]n.d. = not determined.

[d]Fulvic acids from River Tamar.

[e]Fulvic and humic acids from Oyster River.

Liao et al. [LIAO] found in a study of aquatic humic material that only 12 to 17 wt % of the starting material remained after NaOH hydrolysis and 22 to 25 wt % after KMnO4 oxidation. Thus, less than one-third of the original material was accounted for among the structural categories that could be characterized after degradation—making it difficult to generalize about the original macromolecular structure of aquatic fulvic and humic acid. The organic compounds that were identified by Liao et al. [LIAO] in the degradative products included (1) benzene carboxylic acid methyl esters (29 compounds), (2) furan carboxylic acid methyl esters (5 compounds), (3) aliphatic monobasic acid methyl esters (14 compounds), (4) aliphatic dibasic acid methyl esters (14 compounds), (5) aliphatic tribasic acid methyl esters (5 compounds), and (6) (carboxyphenyl)glyoxylic acid methyl esters (8 compounds). The results indicate that aquatic humic substances contain both aromatic and aliphatic compounds. Liao et al. [LIAO] state that "the aromatic rings contain mainly three to six alkyl substituents, and polynuclear aromatic and fused-ring

Table 4. Elemental Composition of Humic Concentrates from Selected Groundwaters. Reprinted by permission [THURMAN].

| | Ash-free and moisture-free basis | | | | | | % | % |
	C	H	N	O	P	S	Ash	Moisture
Laramie-Fox Hills fulvic acid	62.67	6.61	0.42	29.14	0.2	0.44	1.09	2.58
Laramie-Fox Hills humic acid	62.05	4.92	3.Cl	23.45	0.46	0.96	5.12	8.47
Biscayne fulvic acid	55.44	4.17	1.77	35.39	0.2	1.06	0.43	6.75
Biscayne humic acid	58.28	3.39	5.84	30.14	0.22	1.43	0.1	10.38
St. Peter whole	62.33	6.32	0.53	30.20	0.47	0.45	2.16	5.41
Suwannee fulv·c acid	54.65	3.71	0.47	39.28	0.2	0.5	0.95	7.65
Suwannee humic acid	57.24	3.94	1.08	39.13	0.2	0.63	0.56	10.15
Madison whole	56.5	5.84						
Red River whole	61.68	6.78						

structures may also be present. The data suggest that the principal aliphatic segments of the original natural product are composed of relatively short saturated chains (two to four methylene units), and branched structures are apparently present."

The shapes and sizes of humic and fulvic acid particles are known to vary with pH. They tend to aggregate into long fibers or bundles of fibers at low pH, but at high pH they disperse and the molecular arrangement becomes smaller but better oriented. Scanning electron micrographs show that fulvic acid prepared at pH 2-3 and then dried occurs mainly as elongated bundles of fibers. With increase in pH to about 7, the fibers tend to mesh into a finely woven network with a sponge-like structure. For fulvic acid prepared at about pH 8 the structure changes to sheets and at pH 10 homogeneous grains are visible. According to Schnitzer and Khan [SCHNITZER-1978], "one deals here not with chemical structures largely or exclusively composed of condensed rings, but there must be present numerous linkages about which relatively free rotation can occur...humic substances are not single molecules but rather associations of molecules of microbiological, polyphenolic, lignin and condensed lignin origins." Thus, they believe that fulvic acid is made up of phenolic and benzene carboxylic acids joined by hydrogen bonds to form a polymeric structure of considerable stability.

Table 5.   Principal Functional Groups in Humic Substances

Carboxyl	$-\overset{\overset{\displaystyle O}{\overset{\displaystyle \|}{}}}{\underset{\displaystyle \|}{C}}-OH$	Ketone	$-\overset{\displaystyle \|}{C}-\overset{\overset{\displaystyle \|}{C}}{\underset{\displaystyle O}{\|}}-\overset{\displaystyle \|}{C}-$
Carbonyl	$\overset{\displaystyle \|}{\underset{\displaystyle \|}{C}}=O$	Methoxyl	$-OCH_3$
Ester	$-\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle \|}{C}}-O-\overset{\displaystyle \|}{\underset{\displaystyle \|}{C}}-$	Quinone	
Alcoholic Hydroxyl	$-\overset{\displaystyle \|}{\underset{\displaystyle \|}{C}}-OH$		
Phenolic Hydroxyl			

Chemical structures of fulvic and humic acids are depicted in Fig. 1. X-ray analysis and electron microscopy reveal that fulvic acid has a relatively open, flexible structure perforated by voids of varying dimensions that can trap or fix organic and inorganic compounds that fit into the voids, provided that the charges are complementary (Fig. 1a). A suggested structure for humic acid is shown in Fig. 1b. The structures of fulvic and humic acids apparently differ depending upon whether they are derived from marine or terrestrial organic matter. Stuermer and Payne [STUERMER-1976] show that marine fulvic acids are less aromatic and more aliphatic in character and have lower molecular weights than terrestrial fulvic acids. Harvey et al. [HARVEY] propose that marine fulvic and humic acids are crosslinked, autoxidized, polyunsaturated fatty acids (Fig. 2). However, precautions must be taken in observations using electron beam instruments where the humic materials are subjected to high vacuum, anhydrous conditions. Characteristics observed under these conditions may not be appropriate to the natural wet environments to which the observations should be applied.

E.   Origin of Humic Substances in Natural Waters and Soils

As indicated in Section II.B, the composition of total DOC in surface waters that is composed of humic substances ranges from about 60 to 80% and that in groundwaters ranges from as little as 5% to as much as 65%. These dissolved humic substances are mixtures of humic and fulvic acid.   Only a

Table 6. Analysis of "Model" Humic and Fulvic Acid (from means of all data). Copyright 1978 Elsevier Science Publishers. Reprinted by permission [SCHNITZER-1978].

Element (%)	HA	FA
C	56.2	45.7
H	4.7	5.4
N	3.2	2.1
S	0.8	1.9
O	35.5	44.8
	100.4	99.7

Functional Groups (meq/g)	HA	FA
Total acidity	6.7	10.3
CO_2H	3.6	8.2
Phenolic OH	3.9	3.0
Alcoholic OH	2.6	6.1
Quinonoid C=O Ketonic C=O	2.9	2.7
OCH_3	0.6	0.8
E_4/E_6	4.8	9.6

few data seem to be available on the relative proportions of humic acid to fulvic acid in humic substances, although it appears that fulvic acid is the dominant humic species. Thurman [THURMAN-1979] found in one study, for example, that the humic substances in the groundwaters of five aquifers were composed of 60 to 97% fulvic acid, with means of 84% fulvic acid and 16% humic acid. Harvey et al. [HARVEY] report that marine humic substances in the Gulf of Mexico consist of 62 to 98% fulvic acid.

The character of humic substances in groundwaters is different from that in soils and surface waters [THURMAN-1979]. Groundwater humic substances are more aliphatic in nature, less aromatic, less humified, and of lower molecular weight than those in soils and surface waters. They are also enriched in carbon and depleted in oxygen and nitrogen compared to soil humic substances. These differences raise questions about the origin of the dissolved humic substances in groundwaters. Are they derived from terrestrial sources in soils, like the humic substances in surface waters, or do they originate by leaching of particulate humic organic material that is present in groundwater aquifers?

The origin of humic substances in soils is described by Felbeck [FELBECK], who lists the following four hypotheses for the formation of these materials:

(a)

(b)
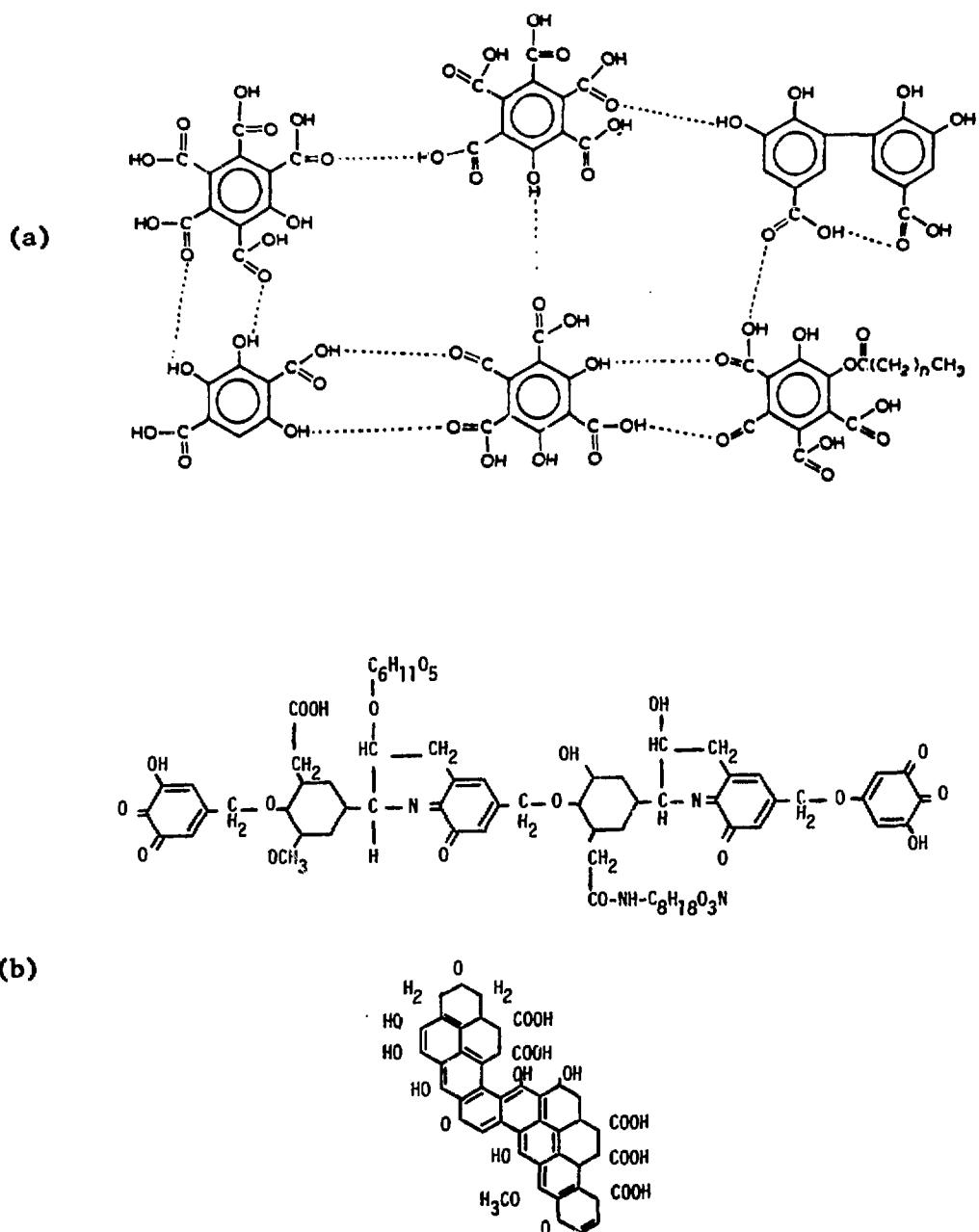
Fig. 1. Chemical Structures for Fulvic and Humic Acids.
(a) A partial structure for fulvic acid. Copy-
right 1978 Elsevier Science Publishers.
Reprinted by permission [SCHNITZER-1978].
(b) A suggested structure for humic acid.
Copyright 1983 SKBF/KBS. Reprinted by
permission [OLOFSSON].

Fig. 2.

Proposed Pathway to Marine Humic
and Fulvic Acids by Oxidative
Crosslinking of Polyunsaturated
Lipids Catalyzed by Ultraviolet
Light and Transition Metals.
Copyright 1983 Elsevier Science
Publishers. Reprinted by
permission [HARVEY].
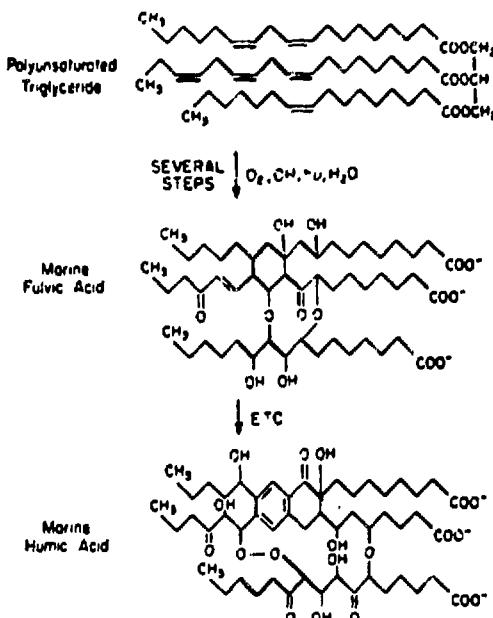
(1)   The plant alteration hypothesis. Fractions of plant tissues that
      are resistant to microbial degradation, such as lignified tissues,
      are altered only superficially in the soil to form humic substances.
      The nature of the humic substances formed is strongly influenced by
      the nature of the original plant material. During the first stages
      of humification, high molecular weight humic acids and humins are
      formed. These are subsequently degraded to fulvic acids and
      ultimately to carbon dioxide and water.

(2)   The chemical polymerization hypothesis. Plant materials are degraded
      by microbes to small molecules that are then used by microbes as
      carbon and energy sources. The microbes synthesize phenols and amino
      acids, which are secreted into the surrounding environment where they
      are oxidized and polymerized to humic substances. The nature of the
      original plant material has little or no effect on the type of humic
      substance that is formed.

(3)   The cell autolysis hypothesis. Humic substances are products of
      the autolysis ("self digestion" or chemical breakdown) of plant and
      microbial cells after their death. The resulting cellular debris
      (sugars, amino acids, phenols, and other aromatic compounds) con-
      denses* and polymerizes by free radicals.

---

*Condensation is an organic chemical reaction in which monomeric
 polymer subunits are joined through intermolecular elimination
 of small molecules such as water or alcohols.

(4) <u>The microbial synthesis hypothesis</u>. Microbes use plant tissue as carbon and energy sources to synthesize intercellularly high molecular weight humic materials. After the microbes die, these substances are released into the soil. Thus, high molecular weight substances represent the first stages of humification, followed by extracellular microbial degradation to humic acid, fulvic acid, and ultimately to carbon dioxide and water.

The common element in all these hypotheses is the suggestion that humic substances in soils start as more complex, high molecular weight organic compounds that are then degraded, probably oxidatively, into lower molecular weight substances, with humic acid forming first and then degrading further to fulvic acid. The differences in groundwater and soil humic substances mentioned above indicate that additional changes in the character of the humic materials must occur either before humic substances get into groundwaters or within the aquifer itself.

One hypothesis to explain the origin of dissolved humic substances in groundwaters is that rainfall percolating through soils leaches and solubilizes humic substances and transports them to the groundwater system. There they presumably undergo further chemical changes within the reducing environment of the aquifer, which may include (1) oxygen depletion by chemical reduction of oxygen-bearing functional groups and (2) removal of oxygen by bacterial degradation [THURMAN-1979]. These changes account for the differences between soil and groundwater humic substances.

A second hypothesis suggests that the humic substances in groundwaters are leached from organic materials that were deposited concurrently with deposition of the sediment making up the aquifer rock. Thurman [THURMAN-1979] offers as possible support for this hypothesis the fact that the humic materials of groundwaters tend to be more aliphatic in character than surface waters or soil humic matter. The more aliphatic character of marine humic substances versus terrestrial humic substances has been established by several investigators [RASHID-1970, STUERMER]. Thurman's reasoning is that because many groundwater aquifers are marine sedimentary rocks, they contain fine particles of marine organic matter trapped among sediment particles; therefore, leaching of marine particulate humic material should result in more dissolved aliphatic organic substances in the groundwaters. One weakness of this argument lies in the fact that terrigenous organic matter can be transported from the land and deposited in marine sediments; thus, the particulate organic matter in marine sediments is not necessarily all of marine origin.

In support of the hypothesis that the DOC of groundwaters may originate by leaching of particulate organic matter within aquifers, Thurman [THURMAN-1979] points out that the carbon and oxygen content of groundwater humic substances is similar to that of kerogen, which now makes up most of the particulate organic matter in sedimentary rocks. Kerogen is disseminated organic matter that originated through complex processes of polymerization and condensation during burial and diagenesis of sediments. Thurman neglects to point out, however, that kerogen is insoluble in nonoxidizing acids, bases, and organic solvents. Presumably, kerogen is also largely insoluble in formation waters because it has survived in sedimentary rocks for hundreds of millions of years in constant contact with formation pore waters. Therefore,

it seems doubtful that the dissolved organic content of groundwater could have originated by solution of kerogen, though it may have originated by solubilization of other types of organic substances in shallow aquifers. The fact that unusually high concentrations of dissolved aliphatic acid anions occur in deep formation waters in association with petroleum accumulations has been attributed to thermocatalytic degradation of kerogen [CAROTHERS]; however, these reactions occur at temperatures between 80 and 200°C and could not account for formation of aliphatic organic substances in shallow aquifers where temperatures are below 80°C, unless high-temperature waters have moved from deeper formations to shallow aquifers.

The hypothesis that DOC in groundwaters originates by solution of organic matter within aquifers also has another weakness. It cannot account directly for the dissolved organic content of groundwaters in volcanic and crystalline igneous rocks that contain no indigenous organic matter. Humic substances dissolved in groundwaters in adjacent sedimentary formations could, of course, migrate into igneous aquifers.

In any case, relatively little work has been done to study the origin of humic substances in groundwaters. Additional research is obviously needed to provide more definitive data on this problem.

F.   Methods for Isolating and Purifying Humic Substances

Before humic substances can be effectively studied, they must be separated from the bulk of other organic and inorganic constituents and concentrated. Methods for concentrating humic substances vary depending upon whether they are being extracted from soils or water. Although our primary interest in this report is in the humic substances in natural waters, specifically in groundwaters, we are including for completeness a short discussion of methods for extracting and purifying humic substances from both soils and waters.

1.   Extraction and Fractionation of Humic Substances from Soils

The first isolation of individual organic compounds from soils was done about 1910 and required extraction of several kilograms of soil to obtain sufficient quantities of organic material for identification [PIERCE]. Since that time, numerous methods for extracting soil organic matter have been introduced. Details of many of these methods are summarized by Schnitzer and Khan [SCHNITZER-1972 -1978]. Other summaries are provided by Dormaar, Felbeck, and Pierce and Felbeck [DORMAAR, FELBECK, PIERCE]. Methods for separating humic substances have included extraction with dilute NaOH, dilute $Na_4P_2O_7$, neutral salts of mineral and organic acids such as Na-pyrophosphate, organic solvents such as acetyl acetone, treatment with chelating (ion-exchange) resins, and ultrasonic dispersion. The method for extracting humic materials by solution in dilute (0.1-0.5N) NaOH is the most widely used technique and was first developed by Oden in 1919 [PIERCE]. Various modifications of the original technique have since been introduced in an attempt to increase the yield and decrease the extent of alteration of the organic matter.

After separation of humic substances from other soil constituents, they are fractionated by various methods into humic acid, fulvic acid, and humin. The basic process for fractionation is shown in Fig. 3. Extraction
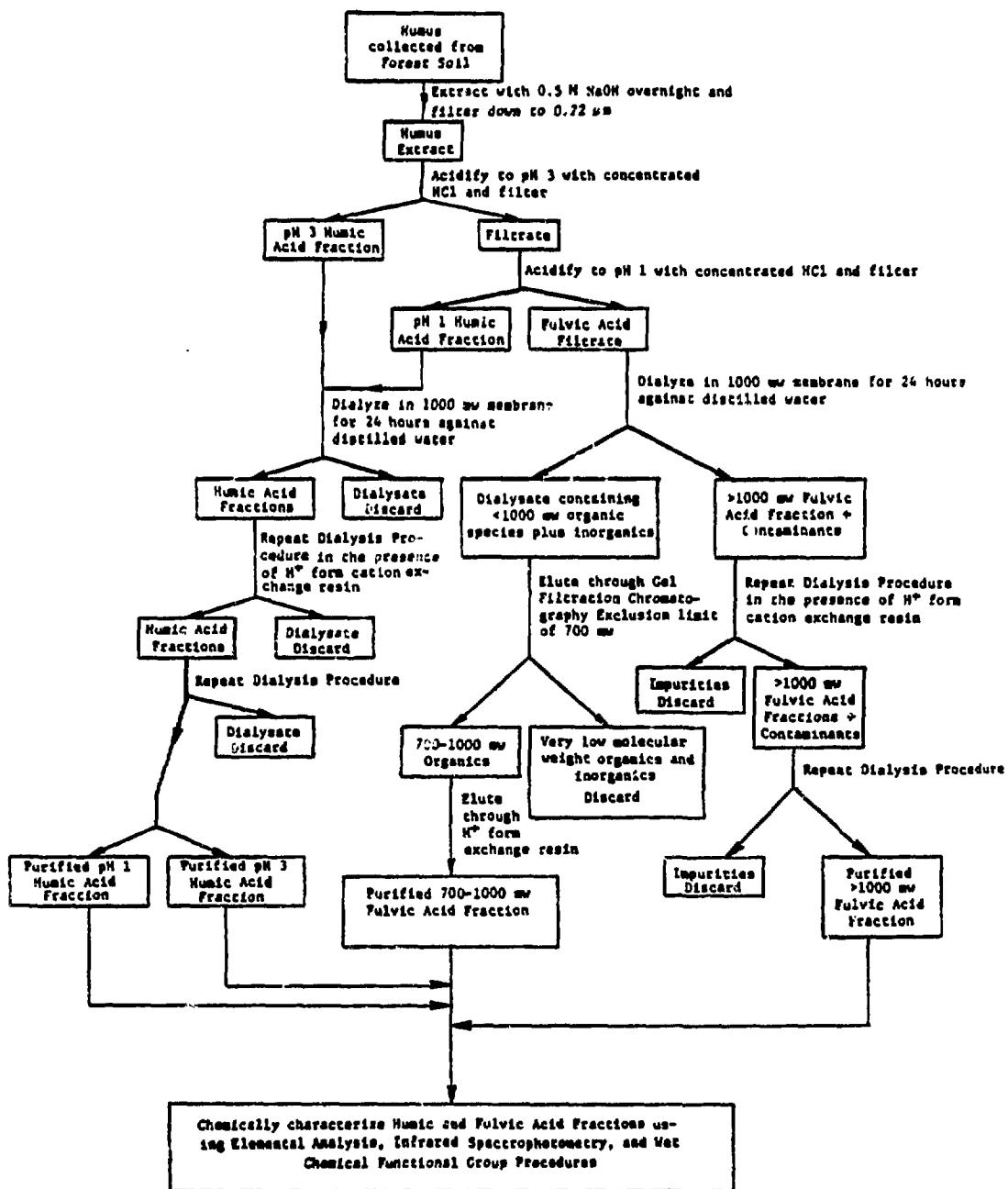
Fig. 3.   Fractionation and Purification Procedures for Humic and
Fulvic Acids.   [MEANS-1982B].

of organic material from soil by treatment with dilute NaOH yields an insolu-
ble humin fraction and a soluble fraction consisting of humic and fulvic acid.
This soluble fraction is separated further by acidifying to pH 1, which causes
the humic acid to precipitate. The humic acid precipitate can then be washed,
purified, and dried to yield a powder of dried humic acid. Dried fulvic acid
can be obtained from the remaining soluble fraction by rotoevaporation or

freeze drying. If desired, the humic acid fraction can be broken down further by extraction with alcohol. More elaborate modifications of this basic extraction and fractionation process that presumably yield better fractionation are described by Pierce and Felbeck [PIERCE].

Other fractionation methods that have been tried include treatment with tetrahydrofuran containing increasing percentages of water, mixtures of dimethylformamide and water, salting out with ammonium sulfate, varying the ionic strength and pH of pyrophosphate and sodium hydroxide extracting solutions, adding increasing volumes of ethanol to alkaline solutions containing humic acids, electrophoresis, and gel filtration chromatography [SCHNITZER-1978].

2. Purification of Soil-Derived Humic Substances

Humic materials separated from soil or sediment may require further treatment to remove remaining inorganic constituents and metal ions that may be complexed with the humic substances. Inorganic constituents can be effectively removed by shaking at room temperature with a dilute solution of HCl-HF (0.5 mL concentrated HCl + 0.5 mL 48% HF + 99 mL H_2O). After shaking for 24 to 48 hours, the acid mixture is removed by filtration and the residue washed with distilled water until free of Cl ions and then dried. Ash content can be reduced in this manner to less than 1.0% [SCHNITZER-1978].

Dialysis has also been used as a method for purifying humic substances. In this process, the dissolved humic material is placed inside a dialysis bag or membrane having a specific molecular weight cutoff, such as 1000. Organic compounds with molecular weights greater than the cutoff value of the membrane remain inside the bag, whereas salts and lower molecular weight compounds are removed. Bound metal ions and salts can also be removed from humic substances by passage over ion exchange resins such as Dowex-50 [NASH-1980].

3. Extracting Humic Substances from Water

The methods for isolating humic substances from water were first developed for concentrating trace amounts of organic substances in seawater. Because of the low concentrations of DOC in seawater and many other natural waters, large quantities of water may have to be processed to obtain desired concentration levels of DOC for analytical purposes. Several methods for extracting humic substances from water have been tried, including freeze concentration and freeze drying, liquid extraction, coprecipitation with various salts, anion exchange, ultrafiltration, and adsorption methods using either charcoal or organic, nonionic resins such as experimental adsorbent (XAD) resins as an adsorbent. The advantages and disadvantages of these different methods of concentration have been summarized by Thurman [THURMAN-1979] and are presented in Table 7.

Because of its ease, speed of application, and high recovery of humic substances, the adsorption method using synthetic nonionic polymers (XAD resins) appears to be the most efficient method for separating dissolved humic substances from water. Large volumes of water can be processed quickly

Table 7. Methods of Concentrating Humic Substances from Water. Reprinted by permission [THURMAN].

Method	Advantages	Limitations
Freeze concentration	1. All nonvolatile organics are concentrated hydrophilic and hydrophobic.	1. All salts concentrated. 2. Slow ~8 L/d. 3. Some loss of organic carbon to ice. 4. Precipitation. 5. Low concentration factors.
Freeze drying	1. High concentration factors.	1. All salts concentrated. 2. Slow 10 L/d. 3. Semivolatiles are lost. 4. Denaturation of humics in presence of salts.
Liquid extraction	1. Method is a precipitation/liquid extraction using glacial acetic acid and isoamyl alcohol. 2. Salts are removed.	1. Solvents not miscible with H_2O do not extract humic substances. 2. Extraction efficiency is questionable. 3. Fulvic acids may not extract.
Coprecipitation with A. $CaCO_3$ B. $Al(OH)_3$ C. $Fe(OH)_3$ D. $Al_2(SO_4)_3 \cdot 18H_2O$ E. $PbCl_2$	1. These methods used in water treatment for removal of organic color. A. Inexpensive. B. ~95% removal by color for very colored waters.	1. Difficulty in large volumes to reclaim and dissolve precipitate. 2. The recovery is questionable in low concentrations of humics as in groundwaters. 3. Excess of salts present.

(contd)

Table 7. (contd)

Method	Advantages	Limitations
Anion exchange A. Strong exchanger	1. Quantitative re- moval of organic acids hydrophilic and hydrophobic.	1. Inorganic anions compete for sites. 2. Elution not quantitative due to matrix interactions.
B. Weak exchanger	1. More specificity for organic acids than strong exchanger. 2. Good elution efficiency.	1. Anions compete. 2. Anions concen- trated with humics.
Adsorption A. Charcoal	1. Very high capacity for adsorption. 2. Fast, easy sample application.	1. Poor elution efficiency due to multiple adsorption sites.
B. Synthetic nonionic polymers	1. Very high capa- cities. 2. Fast, easy sample application. 3. Elution efficien- cies very good. 4. Desalting of sample. 5. Very high concen- tration factors.	1. Aromatic matrix irreversibly absorb ∿25% of sample; there- fore, aliphatic matrices are preferred.
Ultrafiltration	1. Molecular weight separation occurs. 2. Desaltation of high molecular weight organic con- stituents. 3. All organic matter is concentrated by solvent removal.	1. Irreversible adsorption may occur on ultra- filtration membranes. 2. The very low molecular weight constituents are not desalted. 3. Leaching of organic matter from the ultra- filtration membranes. 4. Slow process. 5. Low concentra- tion factors. 6. Fractionation of inorganic salts in organic materials.

and recoveries up to 95% of the humic acid and 75% of the fulvic acid have been reported. The separation of humic substances from water using XAD resins involves two steps:

(1) Adsorption. Water is passed through a column packed with a suitable XAD resin. Humic and fulvic acids are adsorbed onto the resin as the water passes through the column. The XAD resins are nonionic, macroporous organic adsorbents. They are formed by copolymerization and consist of a styrene-divinylbenzene or methyl methacrylate matrix. The pore size and surface area of the resins are a function of the extent of the crosslinking agent. The beads formed consist of many microbeads with pore sizes of about 50 to 250 Å [SIMPSON]. The resins do not contain functional groups and ion exchange does not occur. Trapping or retention of organic solutes on these resin adsorbents occurs by low-energy (1-5 kcal/mol) physical adsorption processes such as hydrogen bonding, van der Waals forces, and dipole-dipole interactions [GUSTAFSON, SIMPSON]. The efficiency of adsorption is influenced by pH and rate of flow of water through the column. Mantoura and Riley [MANTOURA-1975] found that greater efficiency of adsorption occurs at a pH of less than 2.2 and a flow rate of less than 35 bed volumes (column volumes) per hour.

(2) Desorption. Aqueous or organic media are passed through the column to desorb the humic acid and fulvic acid and elute them from the column. Mantoura and Riley [MANTOURA-1975] report that maximum recovery was achieved with 0.2M sodium hydroxide as an eluant; however, a number of other substances can also be used including sodium chloride, ammonium hydroxide, and methanol-ammonia. After the concentrated humic substances are eluted from the column, they must undergo additional treatment to remove the inorganic salts or organic reagents used as eluants and to separate humic acid from fulvic acid.

G.   Methods for Analyzing and Characterizing Humic Substances

Dissolved humic substances can be characterized by both chemical and physical methods. Chemical methods yield data on elemental composition and the composition of oxygen-containing functional groups, and include determination of total carbon, hydrogen, nitrogen, oxygen, sulfur, active hydrogen and total acidity, and acidity of functional groups expressed in meq/g of humic preparation. Specific methods for determining total acidity and the composition of major oxygen-containing functional groups in humic substances are described by Schnitzer and Khan [SCHNITZER-1972]. Schnitzer and Khan [SCHNITZER-1972 -1978] also describe more than 20 physical nondegradative and degradative methods for characterizing humic substances (Table 8). Nondegradative physical methods provide insight into such properties of humic substances as viscosity, ultraviolet and infrared absorbance, shapes of humic acid and fulvic acid molecules, and the chemical structure of humic substances. Degradative methods use oxidative, reductive, thermal, or other degradative techniques to break down the complex structure of humic and fulvic acids into simpler compounds that can be identified and whose chemical structures can then be related to those of the starting materials. Details of these techniques are given by Schnitzer and Khan [SCHNITZER-1972 -1978] and in several

Table 8. Methods for Analysis and Characterization of Humic Substances

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Nondegradative Methods

Spectrophotometry in the UV and Visible Region; Spectrofluorometry
Infrared (IR) Spectrophotometry
Nuclear Magnetic Resonance (NMR) Spectrometry
Electron Spin Resonance (ESR) Spectrometry
X-Ray Analysis
Electron Microscopy and Electron Diffraction
Viscosity Measurements
Surface Tension Measurements
Molecular Weight Measurements
     Vapor Pressure Osmometry
     Ultracentrifugation
     Gel Filtration
Electrometric Titration

Degradative Methods

Oxidative Degradation
Reductive Degradation
Hydrolysis Degradation
Thermal Degradation
Pyrolysis - Gas Chromatography
Radiochemical Degradation
Biological Degradation

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papers that appear in a symposium volume dealing with aquatic and terrestrial humic materials edited by Christman and Gjessing [CHRISTMAN-1983A]. Only a brief summary of some of the more useful techniques is given here.

1.   Spectrophotometry in the Ultraviolet (UV) and Visible Regions

The Beer-Lambert law relating to light absorption states that when monochromatic light traverses a solution, the fraction of the incident light absorbed is proportional to the number of molecules in the light path. Light absorption by a dissolved material is thus proportional to its molecular concentration. The Beer-Lambert law is expressed as

absorbance (or extinction or optical density) $= \log_{10} Io/I = ECL$

where Io = intensity of the incident light,
     I = intensity of transmitted light,
     E = extinction coefficient,
     C = concentration of the substance being investigated, and
     L = path length or thickness of the cell that contains the solution.

The value of E is numerically equal to optical density if C is 1 mol/L and L is 1 cm. Therefore, E is a measure of the intensity of absorption at a given wavelength.

Humic substances generally yield uncharacteristic absorption spectra in the UV and visible regions; however, the ratios at specific wavelengths of optical densities or absorbances of dilute aqueous humic and fulvic acid solutions can be used to characterize humic substances. Soil scientists commonly use the ratio of optical densities or absorbances at 465 and 665 nm for characterization. This ratio is referred to as the E_4/E_6 ratio, and is reported to be independent of the concentration of humic substances but to vary for humic substances derived from different types of soils.

2. Infrared (IR) Spectrophotometry

The vibrations of organic molecules interact with electromagnetic energy to absorb and radiate in the IR region of the electromagnetic spectrum. The main infrared absorption bands of humic substances range from 1050 to 3400 cm^{-1}. The IR spectra provide valuable information on oxygen-containing functional groups and are particularly useful for gross characterization of humic substances of diverse origins. The IR spectra are also useful for detecting changes in the chemical structure of humic substances after various types of degradative treatments.

3. Nuclear Magnetic Resonance (NMR) Spectrometry

Nuclear magnetic resonance is the selective absorption of electromagnetic radiation at the appropriate resonant frequency by nuclei undergoing precession in a strong magnetic field. Thus, NMR spectrometry involves use of an appropriate spectrometer to scan and measure the NMR spectrum of nuclei. The frequency of resonant photons varies slightly for hydrogen in different molecules, and hydrogen in the same molecule in different environments; thus, hydrogen bonded differently can be distinguished in an NMR spectrum. According to Schnitzer and Khan [SCHNITZER-1978], proton-NMR has so far provided relatively little information on the chemical structure of humic materials, but has the potential to provide very useful structural information.

4. Electron Spin Resonance (ESR) Spectrometry

Electron spin resonance is resonance that occurs when electrons that are undergoing transitions between energy levels in a substance are irradiated with electromagnetic energy of a proper frequency to produce maximum absorption. In ESR spectrometry, unpaired or "odd" electrons in paramagnetic substances (substances having a small positive magnetic susceptibility) are measured. Paramagnetic organic compounds, commonly called free radicals, are present in relatively high concentrations in humic substances and may play important roles in polymerization-depolymerization reactions [SCHNITZER-1972]. Therefore, the principal application of ESR spectrometry in the study of humic substances is in studying the nature and reaction of stable free radicals.

5. X-Ray Analysis and Electron Microscopy

Naturally occurring humic substances are largely noncrystalline; however, diffraction patterns of humic acids commonly show atomic spacings of 3.5 Å and those of fulvic acids show spacings of 4.1 to 4.7 Å, indicating the presence of some ordered materials. Electron diffraction also indicates

the presence of crystalline materials in humic substances. Crystallinity in humic substances can be detected only at pH values lower than 2.5, and the d-spacings of these materials resemble those of disordered carbon. Small angle X-ray scattering has also been used to measure the particle sizes of humate materials saturated with sodium.

Electron microscopy permits observations of the shapes and sizes of humic and fulvic acid particles. It has been used to study the structure of these substances and to explore the effects of pH on shape, size, and degree of aggregation of humic acid and fulvic acid particles. A difficulty with using the results of this technique is that the particles are separated from aqueous solution and dried.

6.   Viscosity Measurements

Viscosity measurements of macromolecules in aqueous solutions can provide information about particle sizes or volumes, particle weights, and polyelectrolyte behavior; however, conflicting results have been reported by different workers in applying viscosity measurements to humic substances. The shapes of humic acid particles, for example, have variously been reported to be globular, spherical, elongated ellipses, mixtures of linear and spherical particles, and rod-shaped particles. These different results appear to be caused by investigators using widely differing methods of extraction, separation, and purification of humic materials. If the problem of standardizing techniques can be solved, viscosity measurements offer significant potential for determining some of the important characteristics of humic substances.

7.   Surface Tension Measurements

Humic and fulvic acids are predominantly hydrophilic, but they also contain substantial concentrations of aromatic rings, fatty acid esters, aliphatic hydrocarbons, and other hydrophobic substances. Together, these hydrophilic and hydrophobic substances in humic and fulvic acids cause them to be surface active [SCHNITZER-1978]. Both humic and fulvic acids cause a decrease in the surface tension of waters as pH and concentrations of humic materials increase, and it is thought that hydrophilic oxygen-containing functional groups (CO_2H, OH, C=H) in the humic substances play significant roles in lowering surface tension of waters and in increasing soil wetability.

8.   Molecular Weight Measurements

Schnitzer and Khan [SCHNITZER-1972 -1978] group the various methods for measuring the molecular weights of humic substances into three classes: (1) those methods measuring number-average molecular weights (such as osmotic pressure methods and dialysis), (2) those determining weight-average molecular weights (viscosity measurements, gel filtration), and (3) those measuring z-average molecular weights (sedimentation; e.g., ultracentrifugation). As might be expected, the different methods yield different results for the same materials.

Gel filtration chromatography is the simplest and most convenient method available for determining molecular weight of humic materials, and for these reasons it has been very widely used. Gel filtration involves use of a

long column (a common size is 24 cm x 2.5 cm) packed with an organic gel that has the ability to exclude organic particles larger than a specified molecular weight. A commonly used gel is Sephadex (Pharmacia, Inc.), which is a bead-formed gel prepared by cross-linking dextran with epichlorohydrin. Gels are available in a wide range of exclusion limits or molecular weight cutoffs such as 700, 1500, 100-5000, 500-10,000, and 1000-200,000.

The technique for determining molecular weight by gel filtration requires that a column first be packed with a suitable gel. The solution containing the dissolved humic substances is then passed down the column, which is usually connected to a peristaltic pump. As the solution moves down the column, humic materials are fractionated by molecular weight. A description from the Pharmacia Fine Chemicals Handbook is as follows: "As a solute passes down a chromatographic bed its movement depends upon the bulk flow of the mobile phase and upon the Brownian motion of the solute molecules which causes their diffusion both into and out of the stationary phase. The separation in gel filtration depends on the different abilities of the various sample molecules to enter pores which contain the stationary phase. Very large molecules which never enter the stationary phase, move through the chromatographic bed fastest. Smaller molecules, which can enter the gel pores, move more slowly through the column, since they spend a proportion of their time in the stationary phase. Molecules are, therefore, eluted in order of decreasing molecular size."

The eluant from the column is commonly passed through an inline UV-visible spectrophotometer that continuously monitors the absorbance of the effluent at a wave length (usually 250-420 nm) appropriate to the concentration of fulvic or humic acid expected in the eluant. The eluant then moves on into a fraction collector. The results of gel filtration are generally expressed as an elution diagram that shows the variation of solute concentration in the eluant with the volume of the eluant passed through the column. Comparison of the elution diagram with diagrams obtained with a series of appropriate calibration standards permits determination of the molecular weight ranges of humic and fulvic acids in the sample.

9. Degradation Methods

Degradation methods break down complex humic substances into simpler compounds that can be more easily identified and characterized than the original humic materials. The expectation is that these simpler organic compounds can then be related to the starting humic substances and thus shed light on their structure and composition. Degradation methods include oxidation in alkaline and acidic solutions, reduction, hydrolysis, and thermal, radiochemical, and biological degradation. Degradation products may be further separated and identified by gas chromatography/mass spectrometric techniques [MEANS-1982A -1982B] or other suitable analytical methods. Details of these methods are given by De Haan, Reuter et al., Schnitzer and Khan, and Thurman and Malcolm [De HAAN, REUTER-1983, SCHNITZER-1972 -1978, THURMAN-1983].

III. INTERACTION OF HUMIC SUBSTANCES WITH METALS

A. General Concepts

1. Metal Complexes

Metal-organic interactions have been studied for several decades; however, interest in the complexing of metals with humic substances has intensified since the early 1970s. An extensive literature now exists on this general subject. We make no attempt here to review this large body of published material in its entirety. Rather, we intend simply to abstract and synthesize some fundamental concepts of metal-organic complexing to develop the general background needed to examine the more specific problem of radionuclide-organic complexing. The concept of chemical "complexes" was conceived by the German chemist Alfred Werner in 1893 [MELLOR]. Werner introduced the idea of a metal-centered octahedral chemical structure and wrote, "If we think of the metal as the center of the whole system, then we can most simply place the molecules bound to it at the corners of an octahedron." This concept led to the realization that the valence of an atom and the number of bonds it can form may be different, and that an atom can have both primary and auxiliary valences. The primary valence is now called the oxidation state or oxidation number of the metal; that is, the stoichiometric valence of the element. The auxiliary valence represents the number of atoms bound directly to the central metal atom--called the coordination number. For many metals in the lower oxidation state (+1, +2, or +3), the coordination number is commonly 4 or 6; more rarely it can be 2, 3, 5, 7, 8, 9, 10, or 12. For example, in the hexammine cobalt (III) complex shown in Fig. 4, cobalt has an oxidation number of +3 and a coordination number of 6; in the tetrammine-Cu(II) complex, copper has an oxidation number of +2 and a coordination number of 4.

Fig. 4.
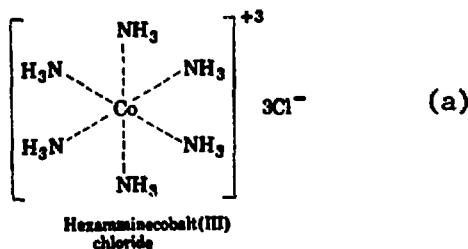
Examples of Metal Complexes.
(a) A coordination number of 6.
(b) A coordination number of 4.
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Hexamminecobalt(III) chloride

Tetrammine-Cu(II) ion
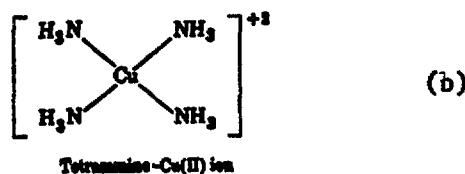
A metal complex is a chemical species that contains a metal atom or ion bonded to a greater number of ions or molecules than would be expected from simple valency considerations. The ions or molecules bonded or coordinated with the metal ion are called ligands. A ligand is any negative ion or polar molecule bound to a metal atom. The actual atom through which a ligand is bonded to a metal is called the ligand atom. Depending upon the charge carried by the metal and its ligands, a metal complex can be neutral, cationic, or anionic. In the metal-ligand bond, the ligand is treated as an electron-pair donor and the metal as an electron-pair acceptor. Two types of bonding are recognized between ligands and metals: (1) covalent bonds in which each of the joined atoms supplies one of the two binding electrons and (2) coordinate bonds in which the metal atom accepts an electron-pair from each nonmetal atom; i.e., the donor atom furnishes both electrons.

Werner also introduced the convention of using square brackets to indicate the entity that functions as a complex. The procedure for writing the formula of a metal complex has now been standardized by an international commission. The symbol for the central metal atom is placed first, followed by formulas of anionic and neutral ligands in that order. The formula for the entire complex or entity (molecule or ion) is enclosed in square brackets, e.g., $[Cu(NH_2 \cdot CH_2 \cdot COO)_2]$.

2. Chelates

Chelates are a special type of metal complex in which the ligands are bonded to the metal through two or more different ligand atoms and, thus, form part of heterocyclic rings in which the metal is one of the members. The word chelate is derived from the Greek chele, meaning claw, in reference to the fact that the ligand ions appear to grip the central ion like a claw (Fig. 5). Metal chelates are defined simply as complexes in which the donor atoms are attached to each other as well as to the central metal ions, forming ring structures. (Note: covalent compounds in which a metal is directly bound to carbon are called organometallic compounds. Organometallic compounds have properties widely different from those of metal complexes and chelates and are not considered further in this report.)

A molecule that acts as a chelating agent must possess at least two appropriate functional groups. The donor atoms of these functional groups must be capable of combining with a metal atom by donating a pair of electrons, which may be contributed by a basic coordinating group such as NH_2 or acidic groups that have lost a proton. Furthermore, these functional groups must be so situated in the molecule that they allow formation of a ring with a metal atom as the closing member. Chelated molecules are more stable than non-chelated metal complexes because the metal ion is gripped more firmly; i.e., the metal atom is more prone to unite with two donor atoms in a ring-forming molecule than with the same atoms in two separate molecules.

The simplest type of chelating molecules are attached to the metal atom by two donor or ligand atoms. Such molecules are called bidentate chelating molecules. That is, a chelating agent that supplies two donor atoms to the metal to form a single chelate ring is bidentate. There are, however, many molecules with three or more donor atoms capable of combining with metal atoms and forming interlocking chelate rings. Based on the number
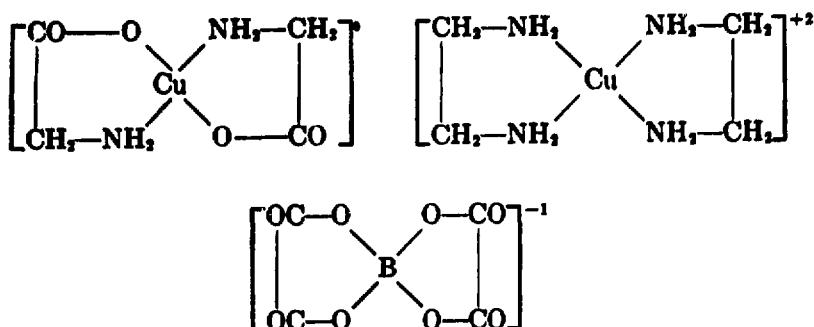
Fig. 5. Structural Diagrams of Chelated Compounds
Illustrating the Ring Structure of Chelates
and the Manner in which the Ligand Ions
"Grip" the Central Metal Ion.
[MARTELL-1952].

of donor atoms capable of combining with a metal atom, these molecules are
called tridentate (or terdentate), quadridentate, quinquedentate, sexadentate,
and octadentate molecules. The coordination number of the metal ion usually
defines the maximum number of groups that can be bound together simultaneously
to the metal ion (Table 9). Atoms known to function as donors in metal com-
plexes are shown in Table 10. Note that simple metal complexes can be joined
by unidentate bonds; however, a chelate cannot be unidentate.

3. Types of Ligands

Numerous types of both inorganic and organic compounds can act as
ligands to form metal complexes. Common examples of inorganic ligands include
the complex anions SO_4^{2-}, HCO_3^-, OH^-, CrO_4^{2-}, and MnO_4^{2-}. Some of the common
types of ligands important in organic chemistry are shown in Table 11. We
are primarily concerned in this report with organic ligands that are capable
of complexing with trace metals and radionuclides. These organic ligands
include synthetic organic chelating agents, such as ethylenediaminetetra-
acetic acid (EDTA) (Fig. 6) and nitrilotriacetic acid (NTA), that are used
routinely in radioactive cleanup and decontamination operations, as well as
natural organic substances that occur in surface waters and groundwaters. The
most important natural chelates are humic and fulvic acid, but organic acids
such as citric, malic, lactic, and tartaric acids may also act as chelating
agents.

B. Stabilities of Metal Complexes and Chelates

1 Stability Constants for Metal Chelates

The tendency toward formation of metal chelate compounds in an
aqueous solution is measured by the chelate formation constant or stability
constant. The magnitude of the stability constant gives a quantitative
indication of the relative stabilities of various metal chelates, and may be
used in conjunction with other data to predict whether or not a metal chelate
compound is likely to form under a given set of conditions.

Table 9. Structural Types of Metal Complexes and Chelates. Copyright 1959 John Wiley & Sons. Reprinted by permission [CHABEREK].

Type of Ligand	Coördination Number			Type of Ligand	Coördination Number		
	2	4	6		2	4	6
Unidentate	A—M—A			Quadridentate			
Bidentate	A—M—A						
Terdentate	A—M—A A			Quinquidentate			
				Sexadentate			

30

Table 10. Donor Atoms in Metal Complexes. Copyright 1964 Academic Press. Reprinted by permission [MELLOR].

			H
C	N	O	F
	P	S	Cl
	As	Se	Br
	Sb	Te	I
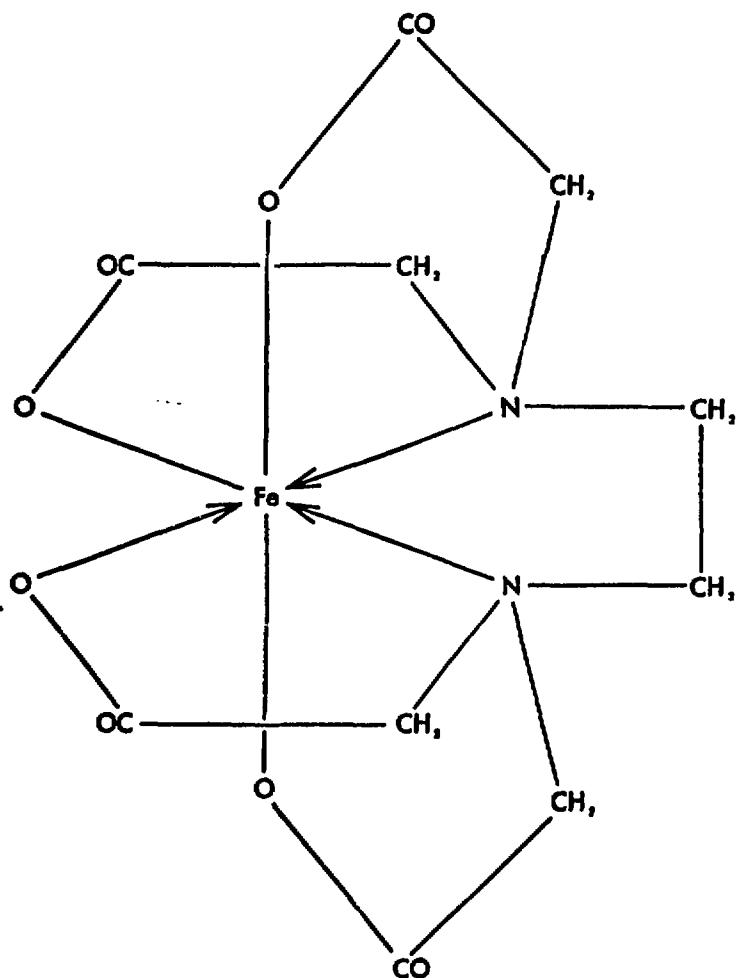
Fig. 6. Structural Diagram Illustrating how Fe is Sequestered and Chelated by Ethylenediaminetetraacetic Acid (EDTA). Copyright 1953 W. H. Freeman and Co. Reprinted by permission [WALTON].

Table 11.   Some Common Types of Unidentate Ligands.
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[HOUGHTON].

Ligand atom		Types of ligand
Carbon	$\overset{-}{C}\!\!\!\diagup_{\diagdown}$	Alkyl carbanions
	$\overset{-}{C}=C\diagup_{\diagdown}$	Alkenyl carbanions
	$^{-}C\equiv C-$	Alkynyl carbanions
	$^{-}C\equiv N$	Cyanide anion
	$^{-}C\equiv\overset{\cdot\cdot}{N}-$	Isocyanides
	$^{-}C\equiv\overset{\cdot\cdot}{O}$	Carbon monoxide
Nitrogen	$:N\diagup_{\diagdown}$	Amines
	$^{-}N\diagup_{\diagdown}$	Amide anions
	$:N=C\diagup_{\diagdown}$	Imines, oximes, azines, hydrazones, unsaturated nitrogen heterocycles
	$^{-}N=C=S$	Isothiocyanate
	$:N\equiv C-$	Nitriles
	$:N\equiv N$	Dinitrogen
Oxygen	$:O\diagup_{\diagdown}$	Water, alcohols, phenols, ethers
	$^{-}O-$	Hydroxide, alkoxide, and phenoxide anions
	$^{-}O_2C-$	Carboxylate anions
	$:O=C\diagup_{\diagdown}$	Aldehydes, ketones, carboxylic acid derivatives
Sulphur	$^{-}S-$	Hydrosulphide, thiolate and thiophenolate anions
	$S=C\diagup_{\diagdown}$	Thiocarbonyl compounds
Halogen	^{-}X	Halide anions
	$:X-$	Alkyl and aryl halides
	$:X\cdot CO-$	Acyl and aroyl halides
Phosphorus	$:P\diagup_{\diagdown}$	Phosphines
	$:P\begin{smallmatrix}O-\\-O-\\O-\end{smallmatrix}$	Phosphites
Hydrogen	^{-}H	Hydride anion

The solution stability of a metal complexed with an organic ligand may be expressed by the equilibrium relationship

$$M + L \rightleftharpoons ML \tag{1}$$
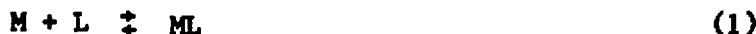
where M refers to the metal ions and L to the organic ligand. The concentration equilibrium constant for this reaction may be defined as

$$K' = \frac{[ML]}{[M] \, [L]} \tag{2}$$

where K' is the experimentally determined stoichiometric stability constant and the brackets indicate that concentrations have replaced activities of the species.

In the formation of a series of metal chelates, the reaction shown in Eq. 1 takes place stepwise:

$$M + L \rightleftharpoons ML \tag{3}$$

$$ML + L \rightleftharpoons ML_2 \tag{4}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \tag{5}$$

The step constants are given by

$$K_1 = \frac{[ML]}{[M] \, [L]} \tag{6}$$

$$K_2 = \frac{[ML_2]}{[ML] \, [L]} \tag{7}$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}] \, [L]} \tag{8}$$

$$K' = K_1 \cdot K_2 \cdot K_3 \ldots K_n \tag{9}$$

K' is the concentration or conditional stability constant, and its value varies with the ionic strength of the solution. It is not the same as the true thermodynamic stability constant (K^t), which is independent of the ionic strength and is given by the relationship

$$K^t = \frac{[ML] \cdot \gamma(ML)}{[M] \, [L] \, \gamma(M) \cdot \gamma(L)} \tag{10}$$

where $\gamma(ML)$, $\gamma(M)$, and $\gamma(L)$ are activity coefficients. With increasing dilution, the activity quotient $\gamma(ML)/\gamma(M) \cdot \gamma(L)$ approaches unity and K' approaches K^t.

The thermodynamic constant (K^t) is related to the standard free energy change (G°) of the reaction by

$$\Delta G^\circ = -RT \ln K^t \tag{11}$$

where R is the molar gas constant (equal to 8.31 $J \cdot mol^{-1} \cdot K^{-1}$), T is temperature in kelvin, and ΔG° is made up of enthalpy (ΔH°) and entropy (ΔS°) terms

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

Conditional stability constants are used to describe quantitatively systems for which activity-coefficient data are inadequate or unknown. Measurement of true thermodynamic stability constants for chelating agents, particularly organic chelating agents, is extremely difficult. Some organic chelates may not be soluble in water at a given pH and the structure of many organic chelates is very complicated and poorly understood. They are commonly ionic, generally contain dipolar ions, and may have dipolar ions and simple ionic groups in the same molecule. Not enough is known about the behavior of such structures to allow evaluation of their activities even in very dilute solutions.

Stability constants can be determined by several different methods based upon a variety of analytical techniques that can be used to measure metal and ligand concentrations [ROSSOTTI]. A method in common use today for calculating conditional stability constants involves application of the Scatchard equation [SCATCHARD-1949 -1956]. A detailed discussion of the Scatchard method and some of its shortcomings is given in Section III.D.6.

2. The Importance of Stability Constants

A stability constant found to be significantly greater than zero is convincing evidence for the existence of a particular complex in solution [ROSSOTTI]. Also, the magnitude of the stability constant is a measure of the bond strength of a metal complex or chelate. Furthermore, once the stability constants for a given system have been determined, it is theoretically possible to calculate the equilibrium concentrations or activities of each of the species present under a given set of conditions. As shown in Eqs. 11 and 12, the equilibrium constant (K) for any reaction is related to corresponding free-energy change by the expression

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

where ΔG°, ΔH°, and ΔS° represent change in free energy, enthalpy, and entropy, respectively. In theory, it is possible to determine ΔH° by measuring the stability constant at a series of temperatures, although in practice it is better to determine ΔH° by direct calorimetric measurements.

3. Factors Influencing the Stability of Metal Complexes

The stability of metal complexes and chelates is affected by several factors. Mellor [MELLOR] grouped these factors into five principal categories:

(1) <u>The size of the chelate rings.</u> Four-membered rings are the smallest rings that have been established with certainty. Five- and six-membered rings are the most common among metal chelates, though structures with higher numbers of members have been postulated. Examples of four-, five-, and six-membered rings are illustrated in Fig. 7. Little quantitative work has been done to establish the effects on stability of ring size, though preliminary work on some chelates suggests that five-member rings may be most stable. Many factors other than the number of members in the ring affect stability, however, and it is difficult to evaluate the influence of ring size alone.

(a)
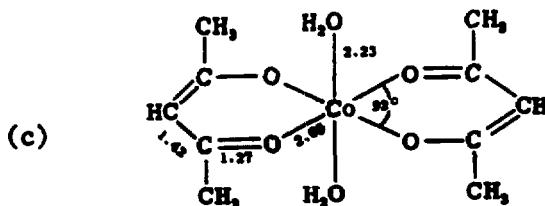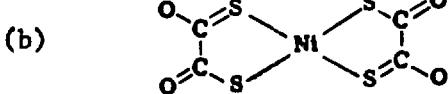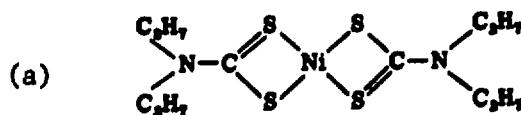
Fig. 7.

Examples of Chelate Rings.
(a) A four-membered chelate ring
[bis (N,N-di-n-propyldithiocarbomato)
nickel(III)]. (b) A five-membered
ring [bis (dithiooxalate-S,S')-
nickelate(II)]. (c) A six-membered
ring [diaquobis (acetylacetonato)
cobalt(II)]. Copyright 1964
Academic Press. Reprinted by
permission [MELLOR].

(b)

(c)

(2) <u>Number of rings (fused rings in multidentate chelating molecules).</u> Among similar chelating agents, those that form the greatest number of chelating rings with a given metal form the most stable complexes (and have the largest stability constants).

(3) <u>The basic strength of the chelating molecules.</u> Both metal ions and hydrogen ions are Lewis acids (e.g., electron acceptors) and there is a resemblance between the combination of a metal ion with a ligand and the neutralization of a base with hydrogen ions. Studies of the possible correlation between basic strength of a series of ligands and the stability of the complexes they form with a particular metal show that for a series of closely related chelating agents, the greater the basic strength, the greater the stability of the metal chelate.

(4) **The effect of substitution in the chelating molecule.** Several
types of substitution reactions are possible in chelating mole-
cules. These include (1) exchange reactions involving either
exchange of ligand or exchange of central metal ion, (2) sub-
stitution reactions involving a net chemical change, and (3)
isomerization reactions. Substitution may alter the basic
strength of the chelating molecule, thereby changing the sta-
bility. Distorting the chelate ring from the normal structure
necessary for bonding resonance may also prevent the ligand
ion or molecule from acquiring the orientation about the
central metal ion most favorable for chelation (steric effect).
The effects of steric hindrance in substituted derivatives
is illustrated in Table 12: the 2-methyl-8-hydroxyquinoline
complexes have lower stabilities than either the
8-hydroxyquinoline or 4-methyl-8-hydroxyquinoline complexes
because the presence of methyl groups adjacent to the nitrogen
donor reduces the accessibility of the 2-methyl-substituted
ligand to metal ions, thus leading to a decrease in stability
of the complexes [BELL].

Table 12. The Effects of Steric Hindrance on Stability Constants, $\lg K_1K_2$.
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Ligand	Metal				
	Mn^{2+}	CO^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
8-Hydroxyquinoline	15.5	19.7	21.4	26.2	18.9
2-Methyl-8-hydroxyquinoline	14.0	18.5	17.8	25.8	18.7
4-Methyl-8-hydroxyquinoline	15.5	20.0	22.3	26	20.2

(5) **The nature of the ligand (donor) atoms and the central metal
(acceptor) atom.** The influence of the ligand atom on stability
is tied closely to the central metal atom and it is difficult
to separate the effects of the two or to make broad generali-
ties about the stability arising from this relationship. Some
central metal atoms are known to form their most stable com-
plexes with ligand or donor atoms of the first element of each
group in the periodic table (N, O, F, etc.), whereas others
form their most stable complexes with atoms of the second or
subsequent elements (P, S, Cl, etc.). For a particular che-
lating agent, the stability of the ligand with a series of
metals appears to be related to the atomic number of the metal.
It has been shown, for example, that the stabilities (stability
constants) of bivalent ions of the first transition series
increase with increasing atomic numbers to a maximum at
copper. Thus, the series goes: Zn < Cu > Ni > Co > Fe > Mn.

The type of bonding also has an influence on complex stability. In a very general way, complexes that are essentially covalently bonded tend to be more stable than those that are ionic. However, notable exceptions to this tendency are recognized; e.g., some of the highly ionic complexes of alkaline-earths that form high-stability complexes.

C. Types of Metal-Organic Interactions

Most investigations of metal-organic complexes have been concerned with their stability, and particularly the effects on stability of environmental variables such as pH, Eh, metal ion and organic carbon concentration, and ionic strength. The complexing behavior of numerous metals has been studied, including Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cs^+, Cu^{2+}, Eu^{3+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, R , Sr^+, and Zn^{2+}. The complexing of radio-nuclides by organic substances has also been investigated, and is discussed in Section IV. The organic substances of principal interest in complexing studies are humic and fulvic acids, which occur in soils, sediments, fresh and marine surface waters, and groundwaters (Sec. II). Most investigators extract humic substances from soils for use in experimental complexing studies because soil humics are the simplest humic substances to extract in large quantities and they are commonly assumed (perhaps incorrectly in some cases) to be similar in character to those found in natural waters. The characterization of humic substances from soils is extensive but by no means complete [SCHNITZER-1978]. Only a few studies have attempted to characterize humic substances from groundwaters [MEANS-1982A, THURMAN-1979].

The types of interactions that occur between metal ions and the organic acids found in natural waters range from complexing reactions to the formation of colloids [MORTENSON]. Many complexes between humic substances and metals have been reported to be chelates. To identify metal-humate chelates, investigators examine the ratio of metal cations complexed per mole of organic material and then compare the types of functional groups found in humic and fulvic acids to those present in other organic acids that have simpler structures and are known to form chelates. The formation of simple complexes and chelates can occur by ion-exchange and surface absorption reactions [MORTENSON]; however, the various processes involved in the formation of metal-humic complexes and the characteristics of the complexes are still poorly understood.

Most investigators who have analyzed and studied the functional groups of humic and fulvic acids conclude that phenolic OH and carboxyl groups [of both phenolic (C-ring) and aliphatic (C-chain) character] are two of the most important functional groups involved in complexation and chelation of metal ions [SCHNITZER-1972]. Knowledge of these functional groups has been applied in modeling studies to investigate metal-organic complexing under natural conditions using organic acids of known composition. Salicylic and phthalic acids (Fig. 8) have been used in such studies as structurally simple analogs for humic substances. Both salicylic and phthalic acids are bidentate ligands (a ligand that has two active functional groups per molecule) where the former contains one carboxyl and one hydroxyl group and the latter contains two carboxyl groups. These organic acids of known composition can be used to simulate the chelation tendency of humic and fulvic acids, which are not easily characterized chemically.

Phthalic Acid
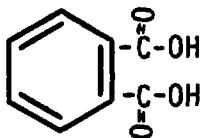
Salicylic Acid

Fig. 8.

Structure of Phthalic and
Salicylic Acids
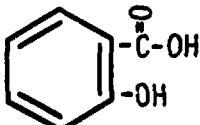
Several workers have discussed the types and stabilities of chelates
that are thought to form between metal ions and natural organic acids. As
an example, Van Dijk [VAN DIJK] reports the results of metal titrations of a
humic acid and discusses possible sources of the H^+ ions that are released
upon addition of Cu^{2+} at both low pH and high initial pH. If chelation
is assumed, one possibility for the formation of a Cu-chelate is
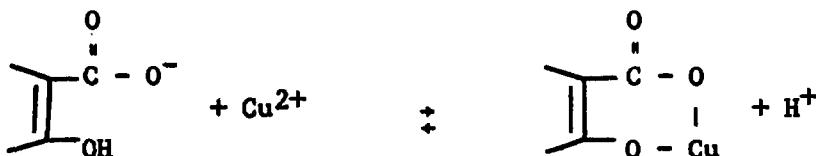
The number of H^+ ions released, measured by the decrease in pH, will depend
upon whether one or both of the functional groups was already protonated. At
higher pH values between 6 and 7, the H^+ release upon addition of Cu salt is
not expected. Van Dijk proposes that the Cu-ion remains hydrated when it
forms the complex with the humic acid and that, at higher pH values, one of
the H^+ ions is released from a water molecule to form a Cu-hydroxy-humate
chelate, such as shown in the following reaction:
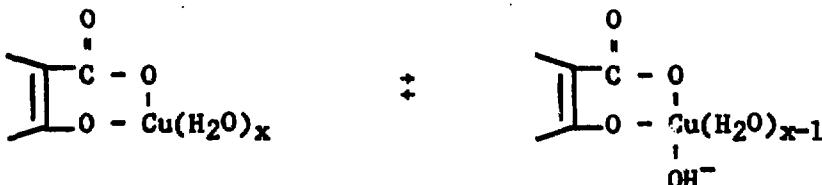
This process of H^+ release should increase the stability of the chelate at
higher pH owing to the newly formed hydroxyl, a conclusion supported by the
work of Stevenson [STEVENSON-1976]. Van Dijk suggests that, if these hydroxy
complexes form in a solution, the chelate stability could be expected to
reflect the increasing tendency of a given metal to form hydroxy complexes
with increasing pH. He determined experimentally that this relationship
holds for Mn, Co, Ni, Pb, and Cu, which increase in metal-hydroxy stability
and humic chelate stability at higher pH, in the order given.

Martell [MARTELL-1971] discusses the chelation of metals by organic acids
in the light of thermodynamic properties. The increased stability of a metal
chelate is directly related to the entropy of the chelate, where increase in
entropy of a solution with an increase in metal ion concentration is reflected
by an increase in the stability of the chelate. Martell demonstrates that a
metal complex with four specific ligands is much less stable than its chelate
counterpart with identical functional groups. One reason for this difference
is the increase in entropy that results from the bridging of negative and
positive ions in a chelate, which increases the concentration of the remaining
free ions in the solution. The coordination number is the number of sites at
which a coordinated ligand can combine with a metal ion. The coordination
number of a metal ion in solution is variable, but is a function of ionic
radius and the charge on the metal, in addition to the characteristics of the
ligand being coordinated. The chelate will become less stable if the coordi-
nation number is exceeded by the number of coordinated ligands. The size of
a chelate ring also affects the chelate stability. The smaller the ring, the
more stable the particular chelate. The enthalpy and entropy effects that
influence solution stability of complexes are given in Table 13.

Table 13. Factors Influencing Solution Stabilities of Complexes.
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permission from [MARTELL-1971].

Enthalpy Effects	Entropy Effects
Variation of bond strength with electronegativities of metal ions and ligand donor atoms.	Number of chelate rings. Size of the chelate ring.
Ligand field effects.	Changes of solvation on complex formation.
Steric and electrostatic repulsions between ligand donor groups in the complex.	Arrangement of chelate rings.
Enthalpy effects related to the conformation of the uncoor- dinated ligand.	Entropy variations in uncoor- dinated ligands.
Other coulombic forces involved in chelate ring formation.	Effects resulting from differences in configurational entropies of the ligand in complex compounds.

Most recent investigations of metal-organic interactions focus on com-
plexing or chelation as the primary uptake reaction of metals by organic
ligands. The extent to which a molecule of humic or fulvic acid may behave
as a colloidal particle in solution is often ignored. Schnitzer and Khan
[SCHNITZER-1972] give a brief discussion of the behavior of organic colloids
in metal binding; however, the formation of metal-organic colloids is fre-
quently overlooked by workers investigating metal-humic complexing.

Colloids are particles less than 10 μm in size that commonly remain suspended in water because their gravitational settling rate is less than 10^{-2} cm/s. "Dissolved" humic substances may be considered as true solutions of macro-ions or negatively charged hydrophilic colloids. Because of their negative charge, one of their properties is coagulation by electrolytes [SCHNITZER-1972]. They can be readily coagulated by Ca^{2+} and Mg^{2+}; therefore, surface waters with high Ca^{2+} and Mg^{2+} (e.g., $>10^{-3}\underline{M}$) contain almost no humic substances (< 1 mg/L) [STUMM]. Some investigators have reported that trivalent ions are more effective in coagulating humic substances than divalent ions, and divalent ions are more effective than monovalent ions. Also, it has been determined that the order of increasing effectiveness of metal ions for coagulating humic acids is $Mn^{2+} < Co^{2+} < Ni^{2+} < Zn^{2+} < Cu^{2+} < Fe^{3+} < Al^{3+}$ [SCHNITZER-1972]. The formation of metal-humic colloids may play an important role under some conditions in the formation of water-insoluble metal humates.

As discussed in Section III.B.3, the stability of metal-organic complexes or chelates is commonly expressed by some type of stability constant. Binding constants, conditional stability constants, successive stability constants, complexing capacities, and distribution coefficients are all experimentally determined values that investigators use in an attempt to describe the tendency of a cation to form a complex with an organic ligand under specified environmental conditions. Ultimately, the purpose of all these experimentally determined constants is to find the thermodynamic equilibrium constants (K^t of Eq. 10) for complexes formed between humic and fulvic acids and metal cations. Realistically, however, it may be impossible to determine true thermodynamic equilibrium constants owing to the chemical complexity of humic substances and the lack of uniformity between humic materials of different origins [PERDUE -1983B]. Chemical characteristics of humic substances vary with the environment (soil, surface water, groundwater, sediment) and origin, i.e., the type of organic material from which the humic substances were derived. For these reasons, humic and fulvic acids cannot be assigned specific elemental compositions or functional groups, but are instead commonly characterized by a range in these properties. Therefore, it is desirable in any study that attempts to evaluate the environmental effects of metal-organic complexes to characterize the natural organic acids from the study area and, if possible, to use these natural materials in experimental modeling studies.

The thermodynamic equilibrium constant is defined for any dissolution reaction between a metal ion as shown in Eq. 10. Conditional stability constants or binding constants (Eq. 2) are simplified forms of the thermodynamic equilibrium constants in that they hold only under given experimental conditions. In effect, all stability constants found between metals and humic and fulvic acids are conditional owing to the fact that these organic acids do not have fixed chemical compositions. Successive stability constants refer to "intermediate" stability constants that, when multiplied together, will give the overall conditional stability constant (Eq. 6-9).

The complexing capacity of a ligand is the maximum number of metal ions that can be complexed by the ligand. The complexing capacity apparently depends upon the coordination number of the ion and the stability of the metal ion complex or chelate. The distribution coefficient is used to describe the

equilibrium concentration of a metal, usually between a liquid and a solid phase. For example, the distribution coefficient between metal ions, expressed in mL/g, in a solution in contact with rock materials such as basalt can be defined as

$$K_d = \frac{\text{metal activity / gram of rock}}{\text{metal activity / milliliter of solution}} \qquad (14)$$

D. Techniques for Studying Metal-Organic Interactions

Many of the common methods used to study metal-organic complexing are reviewed by Schnitzer and Khan [SCHNITZER-1972]. The advantages and disadvantages of the more popular analytical techniques are discussed by Saar and Weber [SAAR-1980]. A few of the more commonly used analytical methods are reviewed in this section to provide a background for understanding how metal-organic interactions are investigated. The methods reviewed include: (1) potentiometric titration, (2) ion-exchange equilibrium techniques, (3) equilibrium dialysis, (4) gel filtration chromatography, and (5) the use of ion-selective electrodes.

1. Potentiometric Titration

This procedure is probably the simplest method for studying metal-organic complexing. It involves titrating a solution containing a known concentration of a specific metal until it reaches its endpoint owing to precipitation of a metal hydroxide. A second titration is then carried out on a duplicate solution to which a measured sample of an organic acid is added. The pH of the duplicate solution will decrease upon addition of the organic acid owing to the displacement of protons in the organic acid by the metal in solution. The shift in endpoint observed in the second titration is taken to be the result of the metal forming complexes with the organic acid. The drop in pH caused by release of H^+ ions is a qualitative indicator of complex formation, and can also be used for quantitative measurements of the stability of the metal complex.

2. Ion-Exchange Equilibrium

The ion-exchange method involves use of an ion-exchange resin as a sorbent for metal ions. Two solutions are used, one with and one without an organic ligand. The solutions are allowed to equilibrate separately with the ion-exchange resin for a specific period of time. The amount of metal ions sorbed from each solution onto the exchange resin is then measured. Distribution coefficients are calculated for each equilibrated solution to establish the ratio of metal ion sorbed onto the exchange resin to metal ion remaining in solution. Distribution coefficients for the solution without the organic ligand are calculated from the relationship

$$\lambda_o = \frac{MR}{[M]} \qquad (15)$$

and those for the solution with the organic ligand by

$$\lambda = \frac{MR}{[M] + [ML_x]} \tag{16}$$

where MR is the concentration of metal sorbed to resin, M is the free metal concentration, and ML_x is the concentration of metal complexed with the organic ligand. The symbol λ_0 is the distribution coefficient for the solution containing no organics and λ is the distribution coefficient for the solution containing an organic complexant. The stability constant for the given conditions will be

$$K = \frac{[ML_x]}{[M] [L]^x} \tag{17}$$

which upon substitution of Eqs. 15 and 16 becomes

$$K = \frac{\lambda_0/\lambda - 1}{[L]^x} \tag{18}$$

or

$$\log K = \log (\lambda_0/\lambda - 1) - X \log L \tag{19}$$

A plot of $\log (\lambda_0/\lambda - 1)$ versus $\log L$ gives $\log K$ as the y-intercept and has a slope of X, the number of moles of ligand bound per mole of metal ion.

3. Equilibrium Dialysis

A dialysis membrane bag having a specified molecular weight cutoff is used to separate two solutions, one containing metal ions and an organic ligand and another containing neither metal ions nor organic ligand. The solution containing the metal and organic ligand is placed outside the bag; the blank solution is put inside the bag. The solutions are allowed to equilibrate through the dialysis membrane. The uncomplexed metal is able to pass freely through the membrane, whereas the complexed metal is retained by the membrane. After the solutions have equilibrated, direct measurements of the free metal that has passed through to the inside of the bag and the complexed metal that remains outside the bag can then be made. The equilibrium concentrations of free and complexed metals allow the strength of the complexes to be calculated.

4. Gel Filtration Chromatography

The principle of gel filtration chromatography is similar to that of equilibrium dialysis except that the "membrane" used in gel filtration takes the form of small beads of dextran gel. A chromatographic column is packed with a suitable gel and a solution containing metal ions and an organic complexant is allowed to pass through the column. As the solution passes down the column, the larger complexed ions are excluded from the small pores of the gel and pass freely and quickly through the column. The smaller free metal ions enter the gel pores and move more slowly through the column. As

the solution is eluted from the column, it can be monitored for ligand concentration by UV-visible spectrophotometry and for metal concentration by suitable analytical techniques. The initial elution volume contains the metal-organic complexes, whereas the volume eluted later contains the free metal ions that were delayed because they passed into the pores of the dextran beads during equilibration. Comparison of the metal-ligand content of the eluted volumes permits the extent of complexing to be evaluated. Additional details of the gel filtration process are given in Section II.G.8.

5. Ion-Selective Electrodes

The ion-selective electrode measures the free metal concentration of a solution through changes in electrical potential between an ion-specific electrode and a reference electrode, just as pH is measured with an H^+-specific electrode. The ion-selective electrode method can be used in conjunction with any of the methods discussed above to measure the free metal concentration. The principal drawback to the method is that it can be applied to the study of only a very limited number of metals, such as Ag, Ca, Cd, Cu, K, Na, and Pb, but not to most trace metals or any of the radionuclides.

6. Calculation of Stability Constants from Experimental Data

The results obtained by the various analytical methods described above are generally used to calculate conditional stability constants. The simplest of these stability constants is calculated by assuming that 1:1 complexes of metal ions to the binding sites of organic ligands are the only complexes that occur (i.e., no chelation takes place) and that the binding site concentrations on the ligand are known. Proceeding from these assumptions, an expression can be written to indicate the reaction between the metal ion and the organic ligand:

$$M^{z+} + HL^{1-z} \rightleftharpoons ML + H^+ \tag{20}$$

The conditional stability constant is then expressed as

$$K = \frac{[ML]\,[H^+]}{[M^{z+}]\,[HL^{1-z}]} \tag{21}$$

On the assumption that pH and $[M^{z+}]$, $[HL^{1-z}]$, or $[ML]$ can be measured, then the conditional stability constant can be calculated from the mass balance relationships for the metal and organic ligand:

$$[M]_T = [M^{z+}] + [ML] \tag{22}$$

$$[L]_T = [HL^{1-z}] + [ML] \tag{23}$$

If the metal-ligand binding ratios are not known, then the Scatchard method [SCATCHARD-1949] for calculating conditional stability constants is commonly used. For example, for the reaction

$$[M] + [L] = [ML] \tag{24}$$

a conditional stability constant can be written with a substituted mass balance relationship similar to that in Eq. 23:

$$K = \frac{[ML]}{[M] \, [L_T - ML]} \tag{25}$$

In the case of the Scatchard method, several binding sites might exist where

$$[L_T] = \Sigma_i \, n_i \tag{26}$$

where n_i is the number of sites of type i on each ligand. Scatchard [SCATCHARD-1949] used these relationships to yield the expression

$$\frac{\bar{\nu}}{[M]} = K_i(n_i - \bar{\nu}) = -K_i\bar{\nu} + K_i n_i \tag{27}$$

where $\bar{\nu} = [ML]/[L_T]$. If experiments are run at a range of concentrations of M, plotting $\bar{\nu}/[M]$ vs. $\bar{\nu}$ will yield a straight line, the slope of which is equal to $-K_i$, the $\bar{\nu}/[M]$ intercept is $K_i n_i$, and the intercept on the axis is n_i (Fig. 9). Scatchard plots may display a second straight line segment with a more gentle slope (Fig. 9) that yields a lower stability constant and is interpreted to indicate binding to "weaker" sites. Thus, two stability constants for a given metal-humic complex are often reported; however, the exact meaning of the two constants is not completely clear. They have been suggested to indicate two different types of binding complexes (i.e., 1:1 and 1:2) [BERTHA]; however, published data appear inconsistent with regard to which of these constants implies complexes of type 1:1 and of type 1:2. Marinsky [MARINSKY] suggests that the different effects arise out of the tendency of humic and fulvic acids to aggregate and form separate phases, rather than indicating 1:1 and 1:2 complexes. Still another interpretation of their meaning is that the different values of the two constants simply represent binding to two different types of functional groups (e.g., phenolic OH vs. carboxylic).

Furthermore, Perdue and Lytle [PERDUE-1983A] have now cast doubt on the validity of conditional stability constants for metal-humic complexes based on application of the two-component Scatchard equation. They point out that, in a complex mixture of ligands, the conditional average stability constant is not a constant at all, but varies with solution composition. This fact raises an important question. Can conditional average stability constants determined at one set of solution concentration values be extrapolated to other experimental conditions? Perdue and Lytle suggest that "...the calculated 'constants' for 1:1 and 1:2 complexes cannot be regarded as anything more than curve-fitting parameters with no chemical significance. While it is indeed possible that 1:1 and 1:2 complexes are formed, it is not possible to determine the relevant average equilibrium 'constant' because they are not constant in multiligand systems." Thus, the Scatchard equation "...while being rigorous for two-component systems, becomes simply an empirical curve-fitting equation with four adjustable parameters when applied to multiligand systems that contain three or more ligands.... The derived constants have little or no chemical significance."

Fig. 9.

Scatchard Plot for the Binding of
Copper(II) by Fulvic Acid at pH
8.0. The linear components of
the curve are the resolved con-
tributions from the "strong"
sites (----) and the "weak"
sites (-.-.). Copyright 1975
Elsevier Science Publishers.
Reprinted by permission
[MANTOURA-1975].
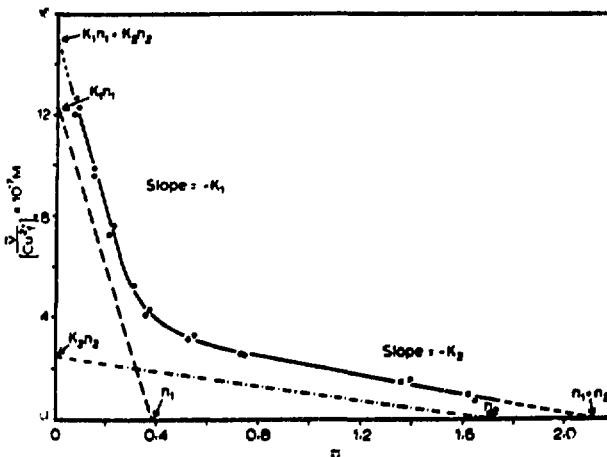
Perdue and Lytle [PERDUE-1983A] suggest that, for complex ligands
such as humic substances, rigorous discrete complexation models can be approx-
imated by continuous models. They propose a statistical-chemical approach
using a Gaussian distribution model with only two curve-fitting parameters,
which they believe shows promise for describing complex multiligand systems.
Such a model could be used to predict the extent of metal complexing at envi-
ronmentally significant metal concentrations from the results of laboratory
experiments that must be carried out at much higher concentrations.

The limitations of the Scatchard plots for analyzing the stability
of fulvic acid complexes are also noted by Dempsey and O'Melia [DEMPSEY].
Commenting on the shape of Scatchard curves, they state that "...there is
continuous change in the slope over the entire length of the curve. If the
curve is enlarged to examine the smaller sections, the same continuous slope
is seen. This indicates that there are many different sites or there is an
interaction between sites - or both are true.... Scatchard plots are useful
for determination of modeling parameters only if the nature and number of
sites or the interactive parameter is known.... Scatchard plots are of
little use for analysis of H-FA reactions, other than to illustrate that
the behavior of FA is complex."

E.   Influences of Metal-Ligand Concentrations and Environmental
      Variables on the Stability of Metal-Organic Complexes

Several recent studies have investigated the relative stability of
metal-humic acid (HA) and metal-fulvic acid (FA) complexes (chelates) as a
function of metal-ligand concentrations and environmental variables such as
solution pH and ionic strength. All the analytical methods for studying
metal-organic interactions described above, in addition to other methods not
discussed here, have been used to determine stability constants for metal-HA
and metal-FA complexes. Owing to the variability of HA and FA types, various

uncertainties introduced by the different analytical methods used, and the variety of laboratory conditions present during experiments, the stability data on metal-HA and metal-FA interactions are complex. Nonetheless, despite some uncertainties in the absolute values of metal-organic stability constants, some general trends in complexing behavior as a function of environmental and concentration variables have been established. For example, many studies have shown that complexing capacity of HA and FA differs with different metal ions at a given pH, and that pH has a strong influence on complexation--which increases for many metals as pH increases. Complexing capacity also generally increases with an increase in HA and FA concentration, but may decrease with an increase in metal ion concentration. These trends are discussed in greater detail below.

1.   Influence of Metal Type

In one of the earlier studies of metal-HA binding, Van Dijk [VAN DIJK] used a titration method to determine the relative stabilities of 11 metal cations with HA at a constant pH of 5. Van Dijk's results revealed two distinct types of cations, those that are weakly bound and those that are more firmly bound to HA. The weakly bound cations are Ba^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, and Zn^{2+}; bond strength between the metal cations and HA increases slightly with each metal of the series in the order shown. The more strongly bound cations, in order of increasing bond strength, are Pb^{2+}, Cu^{2+}, and Fe^{3+}.

Experimental work by several investigators has shown that, under a given set of environmental conditions, Cu^{2+} is complexed more strongly by HA than Cd^{2+} [MANTOURA-1978, SOHN, STEVENSON-1976 -1977, TAKAMATSU]. The cation Cu^{2+} is also complexed by FA more strongly than Cd^{2+} [MANTOURA-1978, RAINVILLE, SAAR-1980, TRUITT-1981A -1981B]. Other studies indicate that Zn^{2+} and Mn^{2+} have binding abilities similar to Cd^{2+} when complexed with HA [HIRATA, MANTOURA-1978, ROSELL, SOHN, STEVENSON-1977, ZUNINO] and FA [HIRATA, MANTOURA-1978, RAINVILLE, SCHNITZER-1970]. The cation Pb^{2+} has been shown to behave more like Cu^{2+} in complexes with HA [STEVENSON-1976 -1977, TAKAMATSU] and FA [SAAR-1980, SCHNITZER-1970]. Zunino and Martin [ZUNINO] found the binding strength of Ca^{2+} and Mg^{2+} with humic substances to be intermediate between that of Cu^{2+}, which is strongly bound, and Zn^{2+}, which is weakly bound. On the other hand, Mantoura and Riley [MANTOURA-1975] found both Ca^{2+} and Mg^{2+} to be only weakly complexed with HA or FA, with stability constants less than that for Zn^{2+}-humic complexes and much less than that for Cu^{2+} complexes.

Some studies have focused on the relationship between metal-HA or -FA binding and the Irving-Williams (I-W) series [IRVING]. The I-W series predicts relative bond strength for divalent metals of the first transition series irrespective of the ligand type or number of ligand molecules. The bond strength varies inversely with the ionic radius and the second ionization potential of the metal concerned. The resulting I-W series is:
Mn < Fe < Co < Ni < Cu > Zn.

Van Dijk [VAN DIJK] studied a series of metals that included those of the I-W series, but found little correlation between the stabilities predicted by the I-W series and the binding of these metals by humic acid. On the other hand, Mantoura et al. [MANTOURA-1978] used gel filtration techniques

to determine that the relative binding strength of complexes between these metals and HA or FA did follow the I-W series. Schnitzer and Hansen [SCHNITZER-1970] and Kerndorff and Schnitzer [KERNDORFF] also found a good correlation between the I-W series (excluding Fe^{2+}, which was not studied) and binding strength of metals with FA and HA.

Kerndorff and Schnitzer [KERNDORFF] allowed solutions of HA containing three trivalent metals (Fe, Al, and Cr) and eight divalent metals (Hg, Pb, Cu, Ni, Cd, Zn, Co, Mn) to equilibrate at varying pH values, and then determined the stability constants for each metal-HA complex. They found that the metals with higher stability constants were able to compete more successfully for the binding sites on the HA molecules. The metals were broken down into three groups according to the relative strengths of their bonds with HA:

Strong: Fe^{3+}, Hg^{2+}

Intermediate: Cu^{2+}, Pb^{2+}, Al^{3+}

Weak: Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}

These results agree very well with those of most previous studies, some of which also considered the relative binding strengths of divalent Mg and Ca. If Mg and Ca are added to this series in their proper positions, the expanded relative stability series for the binding of the common metals with humic substances becomes:

Strong: Fe^{3+}, Hg^{2+}

Intermediate: Cu^{2+}, Pb^{2+}, Al^{3+}

Weak: Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}

2. Type of Organic Matter

Metals are bound relatively weakly by HA and FA compared to binding by some organic pollutants found in the environment, e.g., EDTA [MEANS-1978]; however, humic materials are the most important natural organic substances found in surface waters and groundwaters (Sec. II.B) and, thus, are of great interest in studies of metal-organic complexing. Some studies have examined the relative binding strength of complexes formed with HA versus those formed with FA, and have reported that the binding of metals by FA is stronger than that by HA; however, this assertion is an oversimplified generalization because HA and FA from different environments are known to have different complexing capacities. For example, Mantoura et al. [MANTOURA-1978] compared the binding of copper with HA and FA obtained from several different environments. Their results show that binding capacities vary among humic materials from different sources, but in all cases where the binding capacities of HA and FA from the same general environment were compared, HA was a stronger binder of Cu^{2+} than FA. The stability constants for Cu^{2+} binding with several types of humic materials increased in the order:

soil FA < soil HA < peat FA < peat HA < seawater HM <

lake HM < river HM < marine sediment FA < marine sediment HA

where HM refers to undifferentiated humic matter.

3. Metal and Organic Acid Concentrations

The effects of changes in metal or organic concentration are some-
times expressed as the ratio of the metal concentration to the concentration
of humic organic matter, i.e., [M]/[FA] or [M]/[HA]. Ong et al. [ONG] studied
the stability of five metals (Cu^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+}, Pb^{2+}) with several
types of organic acids, including HA and FA, and found in all cases that
decreases in [M] or increases in [FA] or [HA] (i.e., decrease in [M]/[HM])
tended to increase the stability of the metal-organic complex (colloid).
Saar and Weber [SAAR-1979] found that a decrease in [M]/[FA], produced by an
increase in [FA], increased the stability of Cu^{2+} and Pb^{2+} complexes, while
decreasing Cd^{2+}-FA complex stability. Saar and Weber surmise that the decrease
in stability of the Cd-FA complex with a decrease in [M]/[FA] is due to confor-
mational changes of the FA molecule; that is, a decrease in the apparent size
of the molecule, which results in the blocking of sites on the FA molecule to
which Cd^{2+} is weakly bound at lower [FA]. Both Cu^{2+} and Pb^{2+} ions, which
are bound more strongly than Cd^{2+} at low [FA], apparently overcome the addi-
tional intramolecular forces that occur at higher [FA] and are consequently
more strongly bound with a decrease in [M]/[FA]. Saar and Weber [SAAR-1980]
found that at low [M]/[FA], Cu and Pb are bound to FA with similar strengths,
but as [M]/[FA] increases owing to increase in the cation concentration, the
Pb-FA complex is precipitated from the solution even before the FA complexing
capacity is reached.

Truitt and Weber [TRUITT-1981A -1981B] examined Cu^{2+} and Cd^{2+}
binding in seven natural water samples with DOC concentrations ranging from
6.8 to 12.5 mg/L. They found little or no correlation between changes in
[M]/[DOC] and the relative strength of binding of Cu or Cd. They did not
measure the [HA] or [FA] as percentages of the total [DOC], and concluded
that the low correlations must be the result of unknown fluctuations in the
relative proportions of [HA] and [FA] in the total [DOC].

Kerndorff and Schnitzer [KERNDORFF] used a method of simultaneous
equilibration of several metals with HA to study binding of Fe, Hg, Cu, and
Pb. They report that the difference in bond strength between the typically
strongly bound Fe and Hg and the less strongly bound Cu and Pb became rela-
tively small as metal concentrations were reduced to low levels (low [M]/[HA]).

4. Effects of pH

The influence of pH on binding of metal ions with humic substances
has been examined in numerous studies. With minor exceptions, these studies
show a general increase in stability of metal-humic matter complexes with
increasing pH. Kerndorff and Schnitzer [KERNDORFF] studied HA complexing
(sorption) by 11 metals (Hg^{2+}, Fe^{3+}, Pb^{2+}, Cu^{2+}, Al^{3+}, Ni^{2+}, Cr^{3+}, Cd^{2+},
Zn^{2+}, Co^{2+}, Mn^{2+}) at pH values ranging from 2.4 to 5.8. Their results
indicate that the strength of all the metal-HA complexes increased with

increasing pH. Ong et al. [ONG] found in studies with both HA and FA that the stability of most, but not all, metals investigated increased with increasing pH. Complexes of HA/FA with Cu^{2+} increased in stability from pH 6 to 9, Al^{3+}-HA/FA complex stability increased from pH 4 to 9, and Fe^{3+}-HA/FA complexes increased in stability from pH 5 to 9. Pb^{2+} complexes increased in stability from pH 5 to 7, but decreased in stability from pH 7 to 9, and Zn^{2+} complexes decreased in stability from pH 7 to 9.

Takamatsu and Yoshida [TAKAMATSU] studied Cu^{2+}, Pb^{2+}, and Cd^{2+} binding by HA and found that stability constants for all metals increased as pH increased from 4 to 7. Bresnahan et al. [BRESNAHAN] found that Cu^{2+} complexes with FA in soil and water increased in stability with increase in pH from 4 to 6. Saar and Weber [SAAR-1979] examined the formation of Cd^{2+} complexes with FA derived from soil and water and found that complex stability increased from pH 4 to 8. Truitt and Weber [TRUITT-1981A -1981B] determined that stability of both Cu^{2+} and Cd^{2+} complexes with soil FA increased with increasing pH. Rainville and Weber [RAINVILLE] studied the complexing of soil FA with Cu^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} and observed that the stability of all metal-FA complexes increased with increase in pH from 5 to 7; however, in a study of Cu^{2+} complexing with another soil FA, Ryan and Weber [RYAN] found no significant increase in complex strength with increase in pH from 5 to 7.

5. Effects of Ionic Strength

The ionic strength of a solution is a function of the concentrations of ions in the solution and the charges on the ions.[*] Schnitzer and Hansen [SCHNITZER-1970] studied the effect of ionic strength on the stability constants determined for FA complexes with ten metals (Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Ca^{2+}, Al^{3+}, Mg^{2+}). In each case, an increase in ionic strength caused a decrease in the stability of the metal-FA complex. Regression plots of ionic strength vs. stability constant show that as ionic strength increased from 0 to 0.15, the stability constants of all the metal-FA complexes decreased linearly; however, the metals could be divided into two groups according to the slopes of the regression lines. The metals forming relatively strong complexes (Fe^{3+}, Al^{3+}, Cu^{2+}, Ni^{2+}, Co^{2+}) yielded regression lines with steep slopes, i.e., their stability constants decreased relatively rapidly with increasing ionic strength, whereas the metals that form weaker complexes (Pb^{2+}, Ca^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+}) yielded regression lines with relatively gentle slopes—indicating a slower rate of decrease in binding strength with increase in ionic strength.

Stevenson [STEVENSON-1976] studied the effect of ionic strength on binding of Pb^{2+}, Cu^{2+}, and Cd^{2+} by soil and peat HA. He observed that the stability constants of these metal-HA complexes also decreased with increasing ionic strength. Langford et al. [LANGFORD] demonstrated a very strong inverse relationship between bound (complexed) Cu^{2+} and ionic strength at fixed pH and [FA] (Fig. 10).

[*]$I = \Sigma\, c_i z_i^2$, where I is ionic strength, C is concentration, and Z is ionic charge.
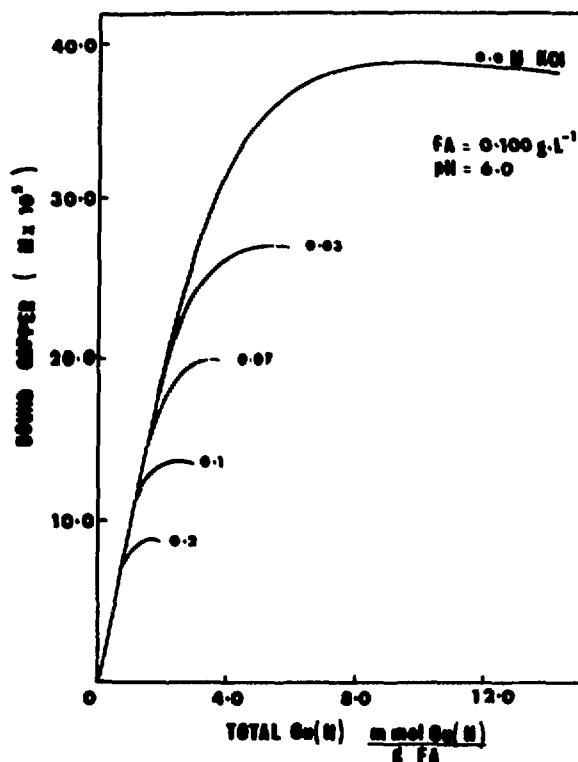
Fig. 10.

Plot of Bound Cu^{2+} vs. Total Cu^{2+}
at Various Ionic Strengths as
Derived from Ion-Selective Elec-
trode Titration of the Fulvic
Acid with Cu^{2+}. [LANGFORD].

The observed decrease in complex stability with increasing ionic
strength apparently reflects the effects of increased competition for binding
sites on the humic materials by other cations in solution. High concentra-
tions of "foreign" cations in solution have the effect of reducing the avail-
able sites for complexation by a particular metal. Owing to the inhibiting
effects on trace metal-organic complexing caused by high concentrations of
Ca^{2+} and Mg^{2+}, Stumm and Morgan [STUMM] questioned the importance of organo-
metallic complexes in natural waters enriched in Ca and Mg. They used thermo-
dynamic data to model the effect of Ca^{2+} on Fe^{3+} complexes with EDTA and
citrate and found that high ratios of $[Ca^{2+}]/[Fe^{3+}]$ in water significantly
reduce the amount of Fe^{3+}-EDTA complexes, which are normally very stable at
lower $[Ca^{2+}]$. A similar effect was observed with Fe^{3+}-citrate complexes,
although a high $[Ca^{2+}]/[Fe^{3+}]$ ratio has less effect on the amount of Fe^{3+}
that complexes with citrate than on the amount that complexes with EDTA. The
difference in complexing behavior of Fe^{3+} with citrate and with EDTA suggests
that the effect on organometallic complexing of a high $[Ca^{2+}]/[$trace metal$]$
ratio is less pronounced with the less strongly binding organic substance (in
this case, citrate). This possibility implies that trace metal-HA/FA complexes
may be less affected by ionic strength than complexes with strong complex
formers such as EDTA.

IV. COMPLEXING OF RADIONUCLIDES BY ORGANIC SUBSTANCES

A. Introduction

In Section III we reviewed the interactions that take place between organic compounds and metals. We examined the factors that influence complexing of various metals by humic substances and developed a base of information on metal-organic complexing to provide a background for understanding the more specific problem dealing with the complexing of radionuclides by humic materials--the main focus of this report. The potential for increased mobility of radionuclides in groundwater systems owing to complexing by humic substances creates concern for the safe disposal of high-level radioactive waste in geologic repositories.

Preliminary evidence suggests that dissolved organic carbon (DOC) in natural waters may influence the sorption behavior of radionuclides (which might leach from high-level waste into groundwater systems) by forming soluble complexes with the radionuclides. These soluble complexes may resist sorption onto rock materials, thereby causing increased mobility of the radionuclides as they migrate through subsurface formations. It is apparent from the discussion in Section III that metal-organic complexing is an extremely complex phenomenon. The complexing capacity of humic substances for various metals is affected by a variety of factors including pH and Eh, the type of metal, concentration of humic substances, concentration of the complexing metal, concentration of competing metal ions and overall ionic strength of the solutions, and the molecular weight range and other chemical characteristics of the organic substances that participate in complexing. In this section, we are concerned with the specific problem of radionuclide-organic interactions, particularly the complexing of actinide metals by organic substances.

We must deal here with two aspects of the complexing problem because there are two categories of mobile organic ligands that may act as complexing agents for radionuclides: synthetic organic ligands and natural organic ligands. Organic ligands in the first category are derived from decomposing organic matter introduced as waste along with radioactive materials into low-level radioactive waste disposal sites. Organic wastes can include a wide variety of products ranging from animal carcasses to paper, rubber and plastic products, and various types of synthetic organic solvents used in nuclear cleanup and decontamination operations. These synthetic organic chemicals include polyphosphates, mono, di-, and tributyl phosphate, aminepolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), nitrilotriacetic acid (NTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), cyclohexanediaminetetraacetic acid (CDTA), and carboxylic acids such as citric, hydroxyacetic, oxalic, and tartaric acids [WIGGINS]. Thus, the first aspect of the radionuclide-organic complexing problem deals with the potential dangers of mobilizing radionuclides in low-level waste disposal sites owing to complexing with synthetic organic substances such as EDTA and NTA. Considerable attention has been focused on this problem since the discovery about 1978 that synthetic organic compounds in some low-level waste sites have already caused significantly enhanced mobility of certain radionuclides.

The second type of organic ligand consists of water-mobile, humic organic constituents, primarily humic and fulvic acids, that occur in natural concentrations in soils, surface waters, and groundwaters. The nature of these organic substances is discussed in detail in Section II. We are particularly concerned with humic substances because their concentrations in natural waters cannot be controlled; thus, they pose a potential problem to disposal of high-level radioactive waste in deep repositories. They may form soluble complexes with actinide elements, such as Am and Pu, that could leach from repositories and thereby promote migration of these actinides through the groundwater system back to the surface and the biosphere. Because of the significance we perceive in radionuclide-humic organic complexing, the remainder of this report focuses on that relationship. We first examine briefly the complexing of radionuclides by synthetic organic compounds. We turn then to the potentially more important problem of radionuclide complexing by natural humic organic substances in surface waters and groundwaters.

B. Complexing of Radionuclides with Synthetic Organic Compounds

The problem of increased mobility of radionuclides in the environment owing to chemical interaction with organic compounds was first identified in low-level radioactive waste disposal sites. Some of these sites are located in areas of moderately high rainfall where transport paths to the groundwater table are short. Such conditions provide an environment in which enhanced mobility of radionuclides owing to organic complexing can significantly affect nuclide transport. Means et al. [MEANS-1978] discovered that the presence of the synthetic organic compounds EDTA, NTA, DTPA, and CDTA increased the mobility of certain radionuclides. Even trace levels ($<$ 1 ppm) of these chelating agents significantly increased the mobility of ^{60}Co, and also affected the migration of the rare earths, radium, and actinide metals such as Am, Cm, and Th. Means et al. concluded that "...wherever EDTA and similar compounds have been introduced into terrestrial disposal sites the aqueous transport of transition metals, rare earths, and transuranics, which characteristically form the most stable chelates, may be augmented."

Since this initial report of radionuclide-organic complexing with synthetic organic compounds, several studies have examined the potential seriousness of such complexing to the safe disposal of low-level radioactive waste. These studies have encompassed both site-specific field investigations and experimental approaches. Examples of site-specific investigations include the work of Cleveland and Rees [CLEVELAND-1981], who studied plutonium complexing in Maxey Flats radioactive trench leachates. These authors found that most of the plutonium was in true solution as a result of forming strong complexes with synthetic organic compounds such as EDTA and DTPA. Weiss et al. [WEISS] also studied Maxey Flats water-soil chemistry and reported that Am, Co, and Pu were made more soluble by the presence of EDTA, whereas Sr and Cs were unaffected under the same conditions. Czyscinski and Kinsley [CZYSCINSKI] used simulated experimental methods to examine the stability of radionuclide-organic complexes in the Maxey Flat system. Their work revealed that Co-DTPA complexes and Co-EDTA complexes persisted in solution under both low redox conditions (-200 mV, NHE[*]) and more oxidizing conditions (0 mV, NHE). They

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[*]Normalized to the hydrogen electrode.

conclude that the temporal stabilities of chelated radionuclides in low redox geochemical environments are not easily predicted from comparisons of appropriate association constants and solubility products, and that empirical information is required to reliably predict the behavior of chelated radionuclides under field conditions.

Means [MEANS-1982B] experimentally investigated the complexing effect of both EDTA and oxalic acid (another complexant used in the nuclear industry) with Cs, Sr, Co, and U, and found that the effect of these organic substances on the sorption and migration behavior of radionuclides varied with different radionuclides. Neither EDTA nor oxalic acid affected the sorption of Cs and Sr onto clay minerals, but EDTA had a strong solubilizing effect on Co, as Means et al. [MEANS-1978] had previously reported. Oxalic acid had little effect on Co, but increased the solubilization of U within the temperature range of 50 to 100°C. Swanson [SWANSON] examined the effects of EDTA, DTPA, oxalate, and citrate (an organic complexant also used in the nuclear industry) on solubilization of Cs, Sr, Ni, Co, and Eu. He found, as Means [MEANS-1982B] had reported, that the effects of the complexants varied widely. No effect of the organic complexants was observed with Cs and Sr; however, pronounced complexant effects were found with Ni/EDTA, Ni/DTPA, Co/EDTA, Co/DTPA, Eu/EDTA, Ni/citrate, and Ni/oxalate.

Clayton et al. [CLAYTON-1981 -1982] conducted batch partitioning experiments to study the effects of EDTA, humic acid, acetic acid, salicyclic acid, and the organic compounds 1-nitroso-2-naphtol and 1,10-phenathroline on sorption of Co, Ru, Cs, and Am onto lake and river sediments. In the 1981 study, EDTA and humic acid were found to solubilize both Am and Co, thereby reducing sorption onto the solids, whereas 1-nitroso-2-naphtol and 1,10-phenanthroline actually increased sorption of Am and Co onto the sediments. The Cs and Ru adsorption behavior was not changed by any of the organic compounds tested. The 1982 study showed that, among all the organic ligands used in the experiment, only EDTA caused solubilization of any of the radionuclides--and then only at ligand concentrations $> 10^{-6}\underline{M}$. The radionuclides ^{57}Co and ^{241}Am were significantly mobilized by EDTA at these greater concentrations; however, ^{137}Cs was not markedly affected by EDTA or any of the other organic ligands. Also, ^{106}Ru was not affected by any of the organic complexants in the experiments with river water, but showed slightly decreased solubilization (increased sorption onto sediment) with all the organic compounds in experiments with lake water. The fact that some of the organic ligands caused increases in adsorption (decreased solubilization) of radionuclides such as ^{57}Co, ^{106}Ru, and ^{241}Am, implies that these ligands are involved in at least two concurrent reactions: (1) complexing the radionuclides, and (2) actively sorbing to the sediment particles. Clayton et al. [CLAYTON-1982] suggest that the relative importance of these two effects may depend upon the ligand concentration. At concentrations less than about $10^{-5}\underline{M}$, the ligands tend to complex or solubilize the radionuclides, whereas at higher concentrations they would have an affinity for the sediment. Thus, depending upon the relative affinity of an organic ligand molecule for radionuclides and sediment particles and the actual concentration of such a ligand molecule, some organic compounds can apparently either increase or decrease the mobility of radionuclides.

These field investigations and laboratory studies show that some synthetic organic compounds are strong complexants for some radionuclides, causing increased mobility of these radionuclides in natural water systems. On the

other hand, these same compounds have little effect on other radionuclides, or actually cause their mobilities to decrease. The synthetic organic compounds that appear to be the strongest complexants are EDTA and DTPA, and the radionuclides that seem to be most affected (i.e., undergo increased mobility) by organic complexing among those tested are Co and Am; those least affected are Cs, Sr, and Ru. The general conclusions that can be drawn from these studies of radionuclide complexing by synthetic organic compounds are that (1) use of alternative decontaminants for nuclear cleanup operations that do not have the complexing properties of EDTA, DTPA, etc. could reduce the risk of radionuclide mobility in low-level radioactive waste disposal sites and (2) prediction of radionuclide-organic complexing on the basis of theoretical considerations is likely to be risky; experimental studies and empirical, site-specific field investigations will be necessary to determine the effects of each type of organic complexant on each radionuclide.

C. Complexing of Radionuclides with Humic Organic Substances

Although the complexing of various substances with trace metals has been under active investigation since Werner proposed the concept of chemical complexes in 1893 [MELLOR], the nature of the complexes that form between natural humic substances and radionuclides has come under scrutiny only very recently. A review of available published literature on this subject reveals that the total number of papers dealing specifically with radionuclide-humic organic complexing is relatively small and that most of these papers were published after the 1960s. Most interest has focused on this field of study since Means et al. [MEANS-1978] reported the effects of synthetic organic compounds on complexing and mobilizing radionuclides in shallow landfills, as discussed in Section IV.B. Their study and other subsequent site-specific studies of radionuclide complexing with EDTA and various synthetic organic compounds have inevitably raised concerns about the possible effects of natural humic organic substances on the mobility of actinide elements and other radionuclides. Published studies of radionuclide-humic organic complexing are of two general types: those dealing with the effects of soil humic substances on radionuclide behavior and those dealing with the complexing effects of humic substances dissolved in surface waters and groundwaters.

1. Complexing of Soil Humic Substances with Radionuclides

Several published studies have examined the effects of soil humic matter on radionuclide complexing and mobility. These studies reveal two opposing tendencies in radionuclide behavior in the soil environment. Under some conditions, certain radionuclides appear to form soluble complexes with the soil humic substances that promote radionuclide mobility in the soil-water system. Other radionuclides, or the same radionuclides under different environmental conditions, can apparently form either insoluble complexes that become bound to soil particles or radiocolloids that precipitate and reduce solubilization, thereby inhibiting removal of the radionuclides from the soil. A few specific studies illustrating these different behaviorial effects are discussed below.

Bondietti et al. [BONDIETTI-1975] investigated the interactions of Pu in various oxidation states with organic substances in soils which were contaminated with trace levels of Pu in the middle 1940s. The nuclide Pu

exists in four oxidation states in solution (III, IV, V, and VI); however, reduction of the higher valence states occurs in the presence of soil humic substances; Pu(IV) appears to be the predominant state that stabilizes in natural environments at pH values above 6.

Soil resin transfer studies by Bondietti et al. showed that a substantial fraction of the Pu in the contaminated soil did not readily desorb under conditions favoring exhaustive removal (Fig. 11). They conclude from these results that Pu forms strong insoluble complexes with soil humic matter and is not readily solubilized by organic resins; that is, the humic materials appear to stabilize Pu in the soil and prevent its mobilization and removal.

Fig. 11.

Resin Extraction of Pu-Contaminated Soil. (Error bars = 96% confidence level.) [BONDIETTI-1975].
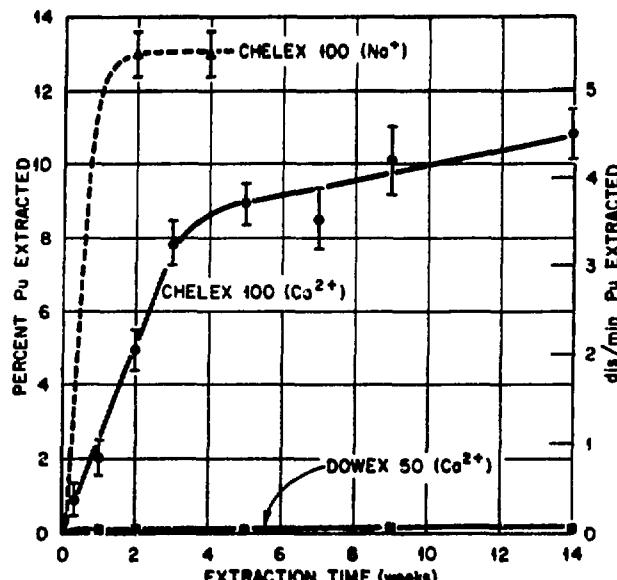
Cleveland and Rees [CLEVELAND-1976] investigated solubilization of Am and Pu in radionuclide-contaminated soils that were allowed to react with fulvic acid solutions. They reported little solubilization in suspensions ranging in pH from 6.5 to 7.5, although a slight solubilization was observed in suspensions adjusted to a pH of 9 by addition of Na_2CO_3. However, at high pH they found it was difficult to discriminate between fulvic acid and HCO_3^-/CO_3^{2-} as solubilizing agents. Their results suggest that Pu forms strong, insoluble complexes with humic substances and that soil humic compounds are not a major factor in the solubilization of Pu and Am in the soils studied. This conclusion may not be totally justified, however, because their experimental procedures did not take into account the possible effects of indigenous fulvic acid in the soil samples, which dissolved during the experiments and yielded as much as 125 ppm of additional fulvic acid to the blank test solutions (assumed to contain no fulvic acid) that were used for comparison in the experiments. Therefore, the effects of fulvic acid on solubilizing Pu and Am could be greater than their results indicate.

Cleveland and Rees suggest that what little solubilization did occur during their experiments was probably due to complex formation and/or colloid

peptization. They observed that the resulting solutions were unstable, and over a period of a few days most of the Pu and Am precipitated, either as the result of colloid coagulation or hydrolysis.

Nash et al. [NASH-1981] studied the complexing of U, Np, and Pu by humic acid and clays. They found that humic acid strongly adsorbs U(VI), Np(VI), and Pu(VI) from aqueous bicarbonate-carbonate media and complexes the IV and VI valence states strongly enough to prevent carbonate complexes. Complexing of NpO_2 with humic acid occurs at both neutral and alkaline pH values. These authors suggest that because humic acids are strongly bound to clays, these results imply probable low mobility of actinide ions in waters contacting humic sediments.

Wiggins and Franz [WIGGINS] summarize and discuss available information on the mobility of organic complexes of radioactive Zr, Nb, Ni, and Tc. They report that relatively little work has been done to characterize the behavior of Zr with soil humic substances, but predict that Zr-organic complexes would be absorbed less by soil than uncomplexed Zr. They suggest that, despite its high stability constants, complexed Nb will be absorbed by soil because of its hydrolysis to insoluble hydrous Nb_2O_5. A few studies of Ni and Co (which is chemically similar to Ni) organic complexes suggest that Ni is solubilized by soil humic substances. Chebotina [CHEBOTINA] reports that plant extracts increase the movement of Co through soil and can also desorb Co from soils. Schnitzer [SCHNITZER-1969] claims that fulvic acid interacts in two distinct fashions with Ni. One interaction appears to involve the formation of a complex incorporating both a carboxyl function and phenolic OH; a second category of complex formation involves only a weakly acidic carboxylic function. The complex involving both carboxylate and phenolic OH in fulvic acid material is more effective in preventing the absorption of Ni by fixed soil constitutents. Very little is yet known about the mobility of Tc in soils, but initial data suggest that it is absorbed only very slightly by soils.

In a series of papers [SHEPPARD-1979 -1980 -1983], Sheppard and his coworkers examined the influence of soil organic matter on the mobility of actinide elements in the soil environment. The organic contents of representative soils from various areas of the United States were determined by the dichromate oxidation method. The soils were then shaken at room temperature (25°C) with distilled water containing ^{241}Am, ^{244}Cm, and ^{237}Np and allowed to equilibrate for periods of time ranging up to six months. Samples were removed periodically for analysis. The supernatant was centrifuged at speeds ranging from 1750 to 7000 rpm before the solutions were analyzed by alpha or gamma counting to determine the activity remaining in solution. The counting data were then used to calculate effective distribution ratios, R^*, defined as

$$R^* = \frac{\text{cpm of actinide per unit volume of supernatant}}{\text{cpm of actinide per unit mass of soil before equilibration}} \qquad (28)$$

This equation differs from that usually used to calculate distribution ratios or distribution coefficients, as shown in Eq. 14.

On the basis of these studies, Sheppard and Kittrick [SHEPPARD-1983] suggest that two reactions of radionuclides with soil humic materials may be important. On the one hand, formation of complexes of actinides such as Am^{3+}, Cm^{3+}, and Np(V) (designated by "M") with fulvic (or humic?) acid (H·Fulv) can be represented by

$$M·Soil + H·Fulv ----> M·Fulv + Soil + H^+ \hspace{2cm} (29)$$

This process forms soluble aqueous complexes that have the potential to increase mobility of actinide elements in the soil-groundwater environment. On the other hand, adsorption and cation exchange of actinides on humic acid in the soil can work in the opposite direction to that of complex formation. Thus,

$$M_{aq} + (H·Hum)_{soil} ---> (M·Hum)_{soil} + H^+ \hspace{2cm} (30)$$

Sheppard and Kittrick [SHEPPARD-1983] caution that these equations should not be taken too literally, because fulvic and humic acids are compounds with rather indefinite compositions.

Perhaps the most interesting result emerging from the research by Sheppard's group was the demonstration that effective distribution ratios are a function of both an ionic component and an actinide-bearing particle component (colloids or radiocolloids). The ionic component is small compared to the particle component and can be subdivided into two principal fractions. (1) Actinide-bearing particles with radii less than 1 nm (equivalent molecular weight 5000). This fraction may include actinide cations and their hydrolysis products (e.g., $AmCl_2$, $Am(OH)_2$), and presumably small humic and fulvic acid complexes with radii less than 1 nm. (2) Actinide-bearing particles with peak molecular weights between 8000 and 50,000. These are humic acid complexes and polymers with radii mainly between 2 and 3 nm. The particle component includes actinide-bearing soil particles (colloidal clay particles?) greater than 3 nm (particularly greater than 10 nm) and humic acid complexes with molecular weights greater than 50,000. The contribution of this component to the calculated distribution ratios depends upon the centrifuging conditions of the experiment. As centrifuging speed is increased from 1750 to 7000 rpm, a progressively increasing fraction of radionuclide-bearing particles is removed from the solution (supernatant); thus, distribution ratios decrease as a function of increasing speed of centrifugation. Distribution ratios were also found to decrease with time, apparently as a result of growth of small particles, flocculation of particles, or redistribution of actinides from small to larger particles.

Sheppard and Kittrick [SHEPPARD-1983] suggest that their data indicate the ionic contribution to the distribution ratio is small and not significant. Also, the contribution from larger actinide particles (radii > 10 nm) is even less important. Thus, intermediate-size soil particles, which are most likely humic acid polymers, are the chief complexing agents of upper horizon soils. Sheppard and Kittrick assumed that humic acid polymers have the approximate composition $[C_{20}H_{12}(COOH)_6(OH)_5(CO)_2]_n$, where n is the number of humic acid monomer units per polymer (polyelectrolyte), and that humic acids have the potential to complex many actinide cations, such as Am(III). Many of the carboxyl and phenol groups must be involved

in the hydrogen bonding that stabilizes the humic acid polymer. They suggest that if the following assumptions are made, (1) half the carboxyl and phenol groups are hydrogen bonded, (2) the molecular weight ranges from 8000 to 50,000, and (3) only carboxyl groups complex metal cations, each humic acid polymer can complex 12 to 75 Am(III) cations; however, many complexing sites under natural conditions in the soil environment are occupied by Ca^{2+}, Fe^{3+}, and other cations, resulting in the complexing of fewer Am(III) cations. Thus, humic acid polymers have variable capacities to complex Am(III) and other actinides depending upon the degree to which complexing sites are occupied by other cations.

Sheppard and Kittrick [SHEPPARD-1983] also considered the transport of actinides in aquifers in the presence of humic compounds. Based on theoretical considerations, they suggest that when the humic acid (or fulvic acid?) concentration is zero, the actinide flow velocity is determined by the actinide distribution coefficient or ratio (K_d); however, in the presence of increasing humic acid concentration, (1) actinide flow velocity is proportional to the humic acid concentration, (2) actinide transport rates are inversely proportional to their respective K_d values, and (3) the magnitude of the actinide flow velocity depends upon the size of the formation complexing constant. These factors are incorporated into the following equation:

$$V(act)/V(H_2O) = B[HA]/(p/o) K_d(0)$$ (31)

where V(act) = actinide flow velocity,
$V(H_2O)$ = aquifer flow velocity,
B = humic acid formation constant,
[HA] = humic acid concentration,
p = soil density, g/cm^3,
o = soil porosity, and
$K_d(0)$ = distribution ratio in the presence of humic acid.

Using a calculated value of 10.4×10^6 for the apparent formation constant of humic acid, Sheppard and Kittrick [SHEPPARD-1983] used the modified FORTRAN computer code GARD to simulate transport of actinides through soil or sand in the presence of various concentrations of humic acid, assuming groundwater flow rates ranging from 0.3 to 3 m/y. The results, shown in Fig. 12, indicate that humic acid has a dramatic influence on rates of actinide transport in groundwater. Humic acid concentrations as low as 10^{-6} mol/L cause a significant increase in the groundwater transport rates of Am(III), and presumably other actinide cations, and confirm the prediction from Eq. 25 (Sec. III.D.6) that the time required for an actinide ion to reach a discharge point from an aquifer is inversely proportional to the humic acid concentration.

The movement of ^{99}Tc through soils was monitored by Balogh and Grigal [BALOGH] using soil column layer chromatography (CLC). Under aerobic conditions, ^{99}Tc occurs as the pertechnetate anion, TcO_4^-. In the soils studied under the short-term ($\sim$24-h) aerobic conditions of the experiment, Tc was found to be quite mobile. These results are in contrast to stronger adsorption reported by Landa et al. [LANDA] in experiments lasting from two to five weeks, which they attributed in part to microbial fixation. Balogh
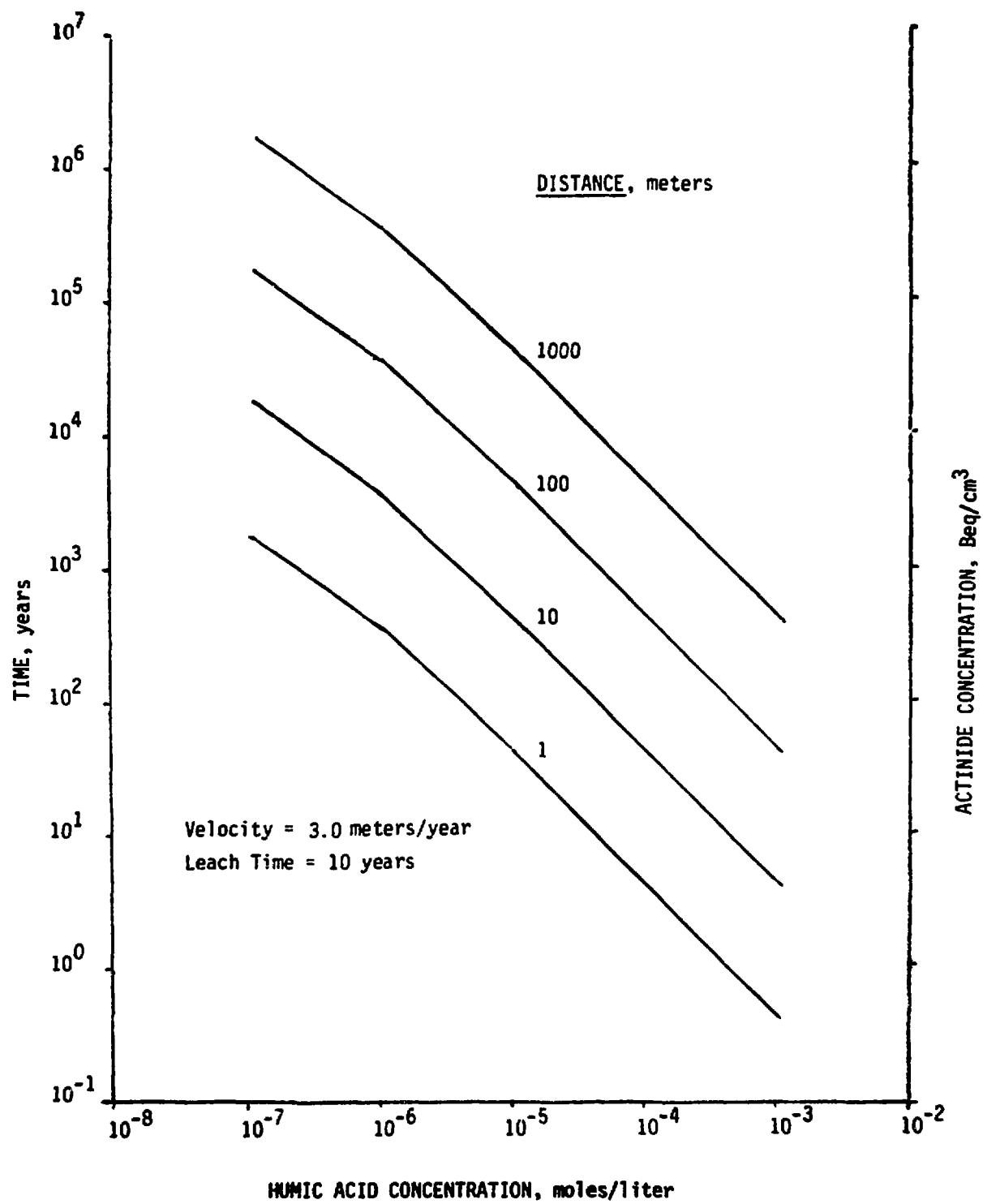
Fig. 12. Influence of Humic Acid on the Rate of Am(III) Transport in Groundwater. [SHEPPARD-1983].

and Grigal interpret the results of their experiment to indicate that, under field conditions, some ^{99}Tc would move with or near the infiltrating waterfront, and that continued rewetting of soil would cause the mobile TcO_4^- anion to move deeper within the soil profile. However, Bondietti and Francis [BONDIETTI-1979] suggest that, under stronger anaerobic conditions, ^{99}Tc would be reduced, leading to fixation and diminished mobility. They propose that under the oxidation-reduction conditions expected for groundwaters not in contact with the atmosphere, TcO_4^- is not the stable state and would be reduced to more insoluble forms such as TcO_2.

Nishita and Haug [NISHITA] used an equilibrium batch technique to study the effects of fulvic and humic acids and inorganic phases in soils on the sorption and extractability of [239]Pu(IV). Comparisons of extractability of Pu were made using (1) untreated soil; (2) soil from which organic matter was removed (fraction I); and (3) soil from which organic matter, free iron oxides, and free silica and aluminum were removed (fraction II). Extractability of Pu was determined by centrifuging both (1) Pu(NO3)4 solutions to which fulvic and humic acids were subsequently added and (2) Pu-dosed suspensions that had been equilibrated with the three types of soil solids for 72 hours. Centrifugation was carried out at 34,858 g for 15 minutes to separate the sorbed and the extractable phases.

The results of Nishita and Haug's experiments indicate that both pH and the presence of humic and fulvic acids have a marked influence on Pu extractability, Pu activity remaining in solution after centrifugation (Fig. 13). Figure 13(a) shows that Pu extractability from Pu(NO3)4 solutions was at a maximum at a pH of about 1.2, where Pu is presumably in ionic form. Extractability dropped to about 40% at pH 3.3 owing to hydrolysis, polymerization, colloid formation, and coagulation, and remained about constant between pH 3.3 and 7.2. Extractability increased abruptly between pH 7 and 8.5, apparently because previously formed coagulates were dispersed (deflocculated) into finer particles that were not carried down by centrifugation. The sharp decrease in extractability again at pH values above 10.7 is apparently the result of the formation of larger particles of some polymerized form of Pu(OH)4.

Figure 13(a) shows that extractability of Pu from Pu(NO3)4 solutions is dramatically changed by the addition of dissolved fulvic acid. Its addition caused Pu extractability to remain at about 90% throughout the pH range of 2.3 to 11.7, indicating that fulvic acids form soluble complexes or chelates with [239]Pu that are stable under both acid and alkaline conditions. The addition of humic acid had about the same effect as fulvic acid pH values above 5, but caused sharply decreased extractability below pH 5. This decrease suggests that Pu was complexed with humic acid, which precipitated out with decreasing pH (humic acid is insoluble at low pH), indicating that Pu-humic acid complexes also are stable under both acidic and alkaline conditions.

The results of the equilibrium batch experiments with the untreated soil are shown in Fig. 13(b) and those for fraction I soil (organic matter removed) are shown in Fig. 13(c). These figures indicate that (1) the presence of the inorganic fraction of the soils significantly decreases extractability (increases sorption) of Pu, particularly at pH values above 3; (2) the

(a)   **(b)**   **(c)**
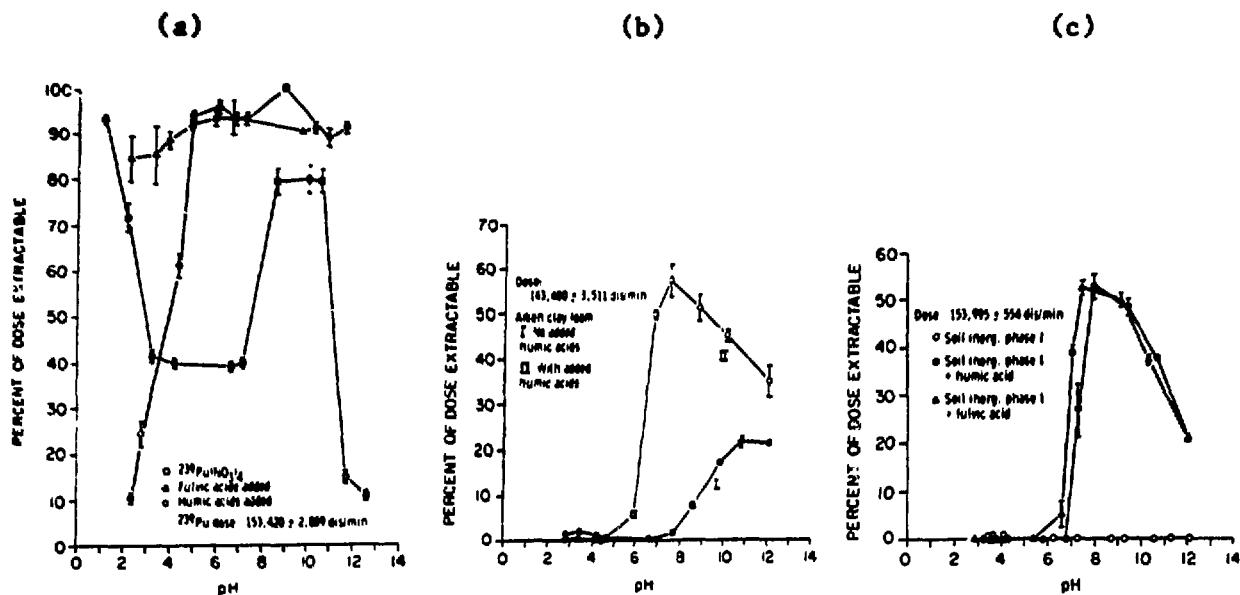
Fig. 13.   Effect of pH on Extractability of ^{239}Pu. (a) From
Pu(NO$_3$)$_4$ solution and solutions of fulvic and humic
acids. (b) From Aiken clay loam (untreated soil)
with and without humic acid amendment. (c) Inter-
action of fulvic and humic acids with inorganic
fraction I of Aiken clay loam. (Standard devia-
tions of triplicate samples are shown by vertical
lines; when <0.5% of dose, they are not shown.)
Copyright 1979 Williams and Wilkins Co.
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addition of fulvic acid and humic acid to the test solutions causes a pro-
nounced increase in Pu extractability (decrease in Pu sorption); and (3)
the magnitude of this increase depends upon the pH and the nature and amount
of organic matter preexisting in the soil. Increase in extractability owing
to addition of humic or fulvic acid was greatest in the pH range from about
to 7 or 8; extractability decreased at higher pH values, apparently owing
to increasing breakdown of the alkali-soluble Pu-organic complex and the
concurrent precipitation of Pu as the hydroxide.

The presence of indigenous organic matter in the untreated soils
organic matter not removed) had the effect of sharply increasing Pu extract-
ability above pH 7 owing to the extraction of alkali-soluble organic matter
fulvic acid?) with which the Pu was associated [curve I, Fig. 13(b)]; how-
ver, compared with the Pu extractability from untreated soils to which no
umic acid was added [curve I, Fig. 13(b)], that from the humic acid-fraction I
ixture (soil organic matter removed, but humic acid added) was markedly
reater above pH 6.82 [Fig. 13(c)]. This effect indicates that the indigenous
rganic matter was sorbed more strongly to the inorganic fraction in the
ntreated soil than the introduced humic acid in the fraction I mixture.
his difference may be due to the shorter time available for the introduced
umic acid to react with the inorganic phase. On the other hand, the Pu

extractability from fraction I soil amended by humic acid addition was generally lower compared with the extractability from the untreated soil to which humic acid was added, and its threshold for sharp increase was shifted to a higher pH level [curve II, Fig. 13(b)]. This difference between fraction I and the untreated soil amended with humic acid indicates primarily the influence of preexisting organic matter on the extractibility of Pu, owing to the fact that the preexisting organic matter will have already occupied many of the sorption sites and will limit the number available to the added organic matter.

Nishita and Haug's experiments [NISHITA] show that plutonium forms complexes or chelates with fulvic and humic acids that are quite stable under normal environmental pH conditions. These complexes have the effect of increasing Pu extractability, and their influence is greatest at higher pH ranges, generally above pH 6. Nishita and Haug suggest that the mobility of Pu in soils under the leaching action of water will depend upon the kinds of organic matter present. "If both soluble and insoluble forms of organic matter are present in the soil under either alkaline or acidic conditions, the contaminating Pu is likely to show relatively high mobility. In this case, the Pu movement will be due mainly to that of the soluble complexed or chelated forms. If the soluble forms of organic matter in the soil are very low in amount, the contaminating Pu is likely to show only small movement. In this case, the movement is likely to be due mainly to the movement of inorganic and/or organic colloidal particles on which Pu is adsorbed and to the movement of insoluble Pu compounds such as PuO_2. In soils devoid of or extremely low in organic matter, the main mechanism of Pu movement obviously must be in the form of inorganic colloidal particles."

2. Complexing of Radionuclides by Dissolved Humic Substances in Surface Waters and Groundwaters

The complexing of radionuclides with humic substances in surface waters and deep groundwaters has been investigated using a broad spectrum of analytical approaches, including both empirical studies and purely experimental techniques. We examine the results of several of these investigations before attempting to draw some broad generalizations and conclusions about the overall significance of radionuclide-organic complexing to the problem of radionuclide migration in the soil and groundwater environment.

Wahlgren and Orlandini [WAHLGREN-1982] studied the partitioning of fallout Pu, natural Th, and U between suspended particulate material and lake water in selected North American lakes. The fallout Pu is present in both the (IV) and (V) oxidation states. The concentration of all these elements was measured in both filtered lake water and suspended solids and the data were used to calculate distribution coefficients for each radionuclide species. The distribution coefficients were then regressed against various limnological parameters such as mean water depth, pH, suspended solid concentration, total alkalinity, and DOC. The distribution coefficients for Pu(IV) and Th were found to show a nearly linear relationship of decreasing distribution coefficients (decreasing sorption of the radionuclide onto the solid phase) with increasing concentration of DOC within the concentration range of about 1 to 100 mg(C)/L (Fig. 14). No significant correlation was established with the other lake parameters. The distribution coefficients for U show a
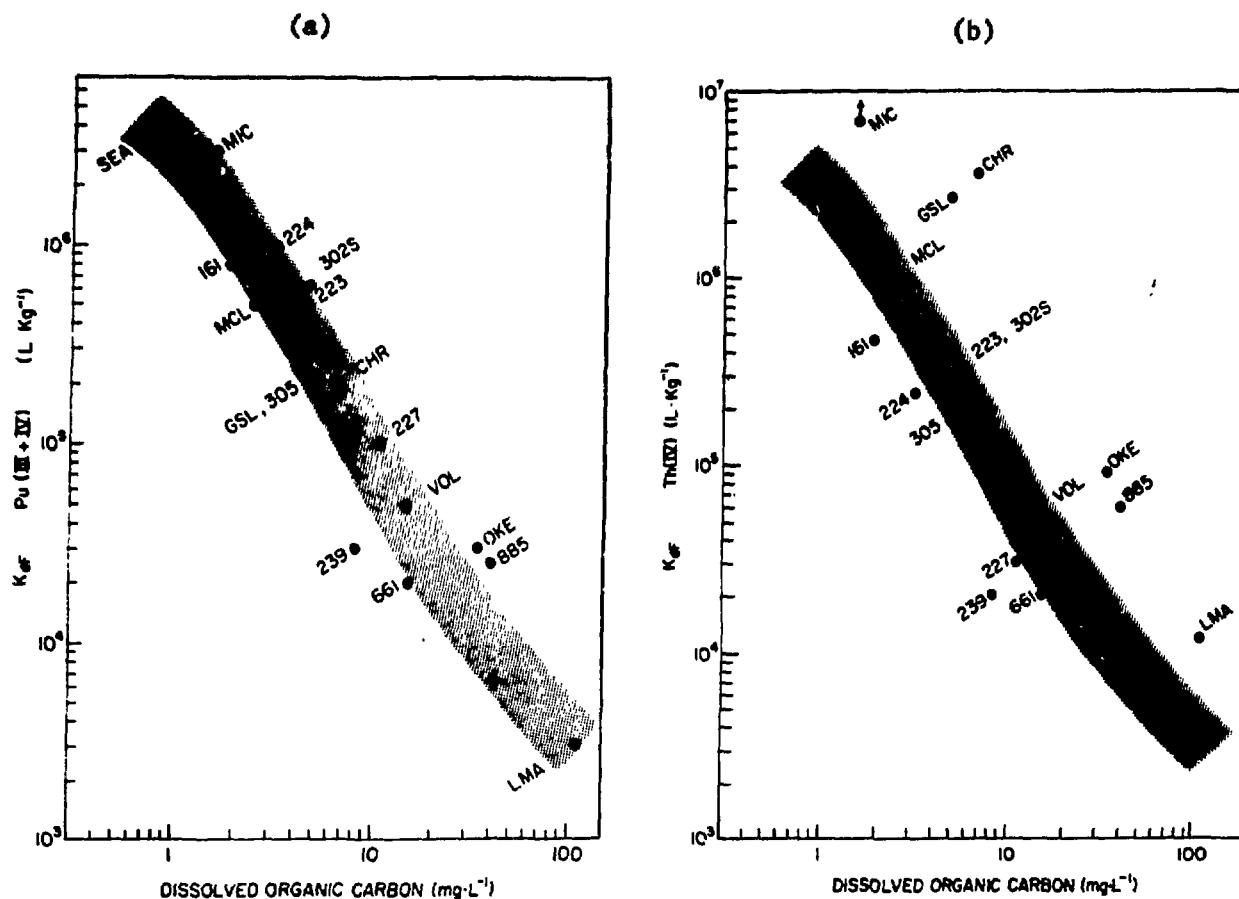
Fig. 14. The Relationship of Distribution Coefficient and Concentration
of Dissolved Organic Carbon. (a) Pu(IV). (b) Th(IV).
[WAHLGREN-1982].

similar trend of decreasing distribution coefficients with increasing concen-
tration of DOC in natural waters with low total alkalinity; however, Wahlgren
and Orlandini suggest that when alkalinity is high and pH exceeds 7.5, alka-
linity rather than DOC appears to control the adsorption behavior of U.

Orlandini [ORLANDINI] reported the results of a similar study of Am
behavior in lake waters. Orlandini calculated a distribution coefficient
based on the ratio of the Am concentration on the < 35- to > 0.45-μm suspended
particulates (dried) to the Am concentration in water. Values of the coeffi-
cient were plotted against the various limnological parameters, including DOC
concentration, pH, and alkalinity. A strong inverse relationship was demon-
strated between DOC concentration and the distribution coefficients--indicating
increased solubilization of Am with increasing DOC concentration. Except for
a possible correlation with high alkalinity values (>300 mg/L $CaCO_3$), no
significant correlation was found with any other limnological parameter.

Nelson et al. [NELSON-1980] examined the effect of DOC on Pu
mobility in certain oligotrophic lakes (lakes with oxygen-rich lowermost
water layers). The dissolved Pu in these lakes is primarily in the oxidized
form [presumably as Pu(V)], which is more weakly sorbed onto solids than the

reduced form [Pu(IV)]. Some Pu(IV) is present in all lakes studied, however, and the apparent solubility of this reduced form varies markedly from lake to lake.

The partitioning of Pu(IV) between lake water and suspended solids was examined by determining a distribution ratio (K_d), which was calculated by dividing the measured concentration of ambient $^{239,240}Pu(IV)$ sorbed to suspended solids (fCi/kg) by the measured concentration of $^{239,240}Pu(IV)$ in solution (fCi/L). Nelson et al. [NELSON-1980] found that the apparent solubility of Pu(IV), as measured by K_d, varied among different lakes as a function of the concentration of DOC in the lakes, but did not appear to be related to the concentration of inorganic constituents in the water. The relationship of DOC to K_d values is illustrated in Fig. 15, which also includes K_d values derived from the results of laboratory experiments in which various natural waters were spiked with ^{237}Pu and equilibrated with aliquots of a single sediment type.
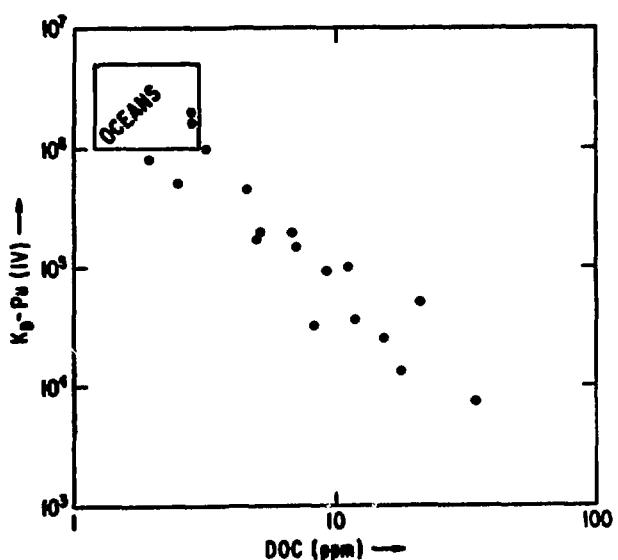
Fig. 15.

Variation of Distribution Ratio as a Function of Ambient Dissolved Organic Carbon Concentration for Several Natural Waters (o represents field measurements, ● represents laboratory equilibrations). [NELSON-1980].

Nelson et al. [NELSON-1980] also conducted several experiments in which K_d values were measured as a function of DOC concentrations that had been adjusted to specific levels. The organic substances used in these experiments were collected from natural waters by ultrafiltration through 1000 mol wt cutoff membranes. Portions of these organic concentrates were then combined with the corresponding ultrafiltered water to produce a series of waters assumed to differ from the original waters only in their DOC concentrations. These waters were spiked with ^{237}Pu tracer, an aliquot of sediment (~40 mg/L) was added, the systems were equilibrated for a week, and the K_d for the reduced Pu was determined. An example of the results of these experiments is shown in Fig. 16. In this example, the DOC content of the water has a pronounced inverse effect on sorption of Pu(IV) even at concentrations less than 1 mg(C)/L. Nelson et al. found, however, that the effects of DOC concentration varied among lakes. In experiments with some lake waters, the
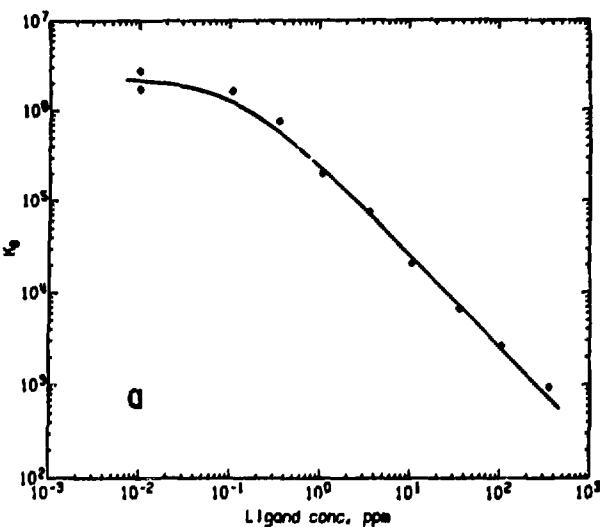
Fig. 16.

Variations of Distribution Ratio
as a Function of Dissolved
Organic Carbon Concentration.
(a) Okefenokee Swamp. (b) Lake
Michigan. [NELSON-1980].
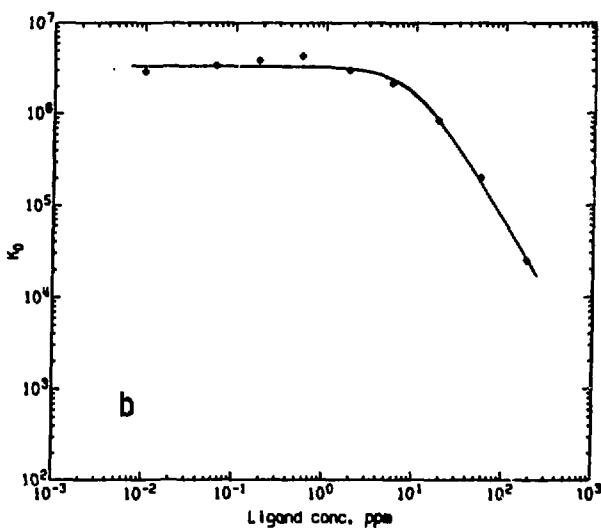
DOC caused a decrease in K_d values only at concentrations well above 1 mg(C)/L.
They link these variations in the effects of DOC concentration to differences
in the stability constants of the Pu(IV)-organic complexes, although it is not
clear what causes the variations in stability of the complexes.

In evaluating Fig. 16, it should be noted that ultrafiltration tech-
niques are now known to fractionate major inorganic constituents of water such
as Ca, Mg, F, and S, as well as the total organic carbon [BOGGS-1984B, KIM].
These results suggest that the organic molecules may exist as a complex with
large fractions (~30%) of major constituents of groundwaters. In any case,
the concentrate prepared by Nelson et al. may include concentrates of inorganic
elements as well as the total organic carbon. The inorganic elements, whether
complexed or not with the organic molecules, may contribute to the results
depicted in Fig. 16.

In a subsequent paper, Nelson et al. [NELSON-1982] determined that two types of Pu-organic complexes were formed, one with one ligand per Pu atom, and the other with two ligands. They developed an equation assuming competitive equilibrium between Pu(IV) and soluble complexing ligands and between Pu(IV) and a solid adsorber:

$$\frac{1}{K_d} = \frac{1}{K_d^{\ o}} + \frac{K_1}{K_3} [DOC] + \frac{K_2}{K_3} [DOC]^2 \tag{32}$$

where

K_1 and K_2 are conditional stability constants for the 1:1 and 2:1 complexes of Pu with organic ligands, respectively;

K_d is the observed distribution ratio when organic matter is added;

$K_d^{\ o}$ is the distribution ratio of uncomplexed ions and all low molecular weight inorganic and organic complexes (<1000 mol wt; i.e., very low DOC concentrations); and

K_3 is the conditional stability constant for the association of Pu with the solid adsorber.

The absolute values of K_1, K_2, and K_3 cannot be obtained from these experiments; however, because the value of K_3 is presumably the same for all experiments, the ratios of K_1/K_3 and K_2/K_3 can be determined. Thus, the relative complexing power of colloidal DOC from two bodies of water can be compared by comparing the values of K_1/K_3 and K_2/K_3 for the two waters. High values of K_1/K_3 indicate strong 1:1 complexes of Pu with DOC (1 mol DOC/Pu atom) and lower values indicate relatively weaker complexes. This relationship means that dissolved organic substances would cause a much greater decrease in K_d in waters with high K_1/K_3 ratios than in waters with low ratios. Similarly, the value of the K_2/K_3 ratio indicates the relative importance of 2:1 complexes of Pu with DOC (2 mol DOC/Pu atom).

Nelson et al. [NELSON-1982] found that an increase in pH causes a decrease in K_1/K_3 values but an increase in K_2/K_3 values, and vice versa. That is, an increase in pH causes a decrease in the stability constants for Pu(IV)-organic complexes but an increase in the stability constants that measure the strength of the association of uncomplexed Pu(IV) with the solid absorber. Because these changes are offsetting at moderate DOC concentrations, the principal effect of pH change is to alter the type of complex ion formed, and causes only minor changes in K_d.

Li et al. [LI] used dialysis techniques to investigate the effects of pH and U concentration on the interaction of U(VI) and U(IV) with fulvic, humic, and tannic acids. The effect of pH on U-organic complexing was studied by preparing solutions containing 20 mg/L of humic, fulvic, or tannic acid spiked with either 50 ng/mL U(VI) in 0.01M KNO$_3$ solution or 50 ng/mL U(IV) in 0.01M NaCl solution. The pH of the solutions was varied from 2 to 9 by adding $\overline{H}NO_3$ or NaOH, as appropriate. The solutions were placed inside

dialysis bags (having a cutoff of 3500 mol wt) for 24 hours to separate by size the U(VI) or U(IV) species complexed with humic, fulvic, or tannic acid (larger size) from the inorganic complexes of U(VI) and U(IV) (smaller size).

The results of these experiments are shown in Fig. 17; a high value for % U dialyzed indicates a low degree of complexing with organic ligands. Note that pH has a very pronounced effect on complexing and that complexing increases with increasing pH, with a particularly sharp increase taking place within the pH range of about 3 to 6. Note also that humic acid (HA) can bind uranium at lower pH values than fulvic acid (FA) or tannic acid (TA). This difference is related to the difference in pK_a values of the humic, fulvic, and tannic acids, which are reported by Guy and Chakrabarti [GUY] to be about 4 for HA, 5 for FA, and 6 for TA. [pK_a is the dissociation constant for the degree of dissociation represented by a.] If the stability constants of the U(VI) complexes of HA, FA, and TA are similar, then the magnitude of and difference in the pK_a values (4,5,6) would indicate that at low pH ($\sim$4), the amount of free U(VI) ion would follow the order of the pK_a; i.e., pK_a: TA > FA > HA, which was experimentally observed as shown in Fig. 17(a). That is, the percentage of U(VI) dialyzed (the amount of free, uncomplexed ion) is greatest for FA and least for HA. Above pH 5, the concentration of free ions is small (most of the U(VI) is complexed) for the three acids and increases in the order FA > HA > TA, which may reflect the order of inherent stabilities of the complexes with U(VI). Fig. 17(b) shows that very similar results were obtained for U(IV). A comparison of the curves in Fig. 17(a) with those in Fig. 17(b) indicates that U(IV) forms stronger complexes with HA, FA, and TA than U(VI), especially at low pH (4 or less).

(a)   (b)
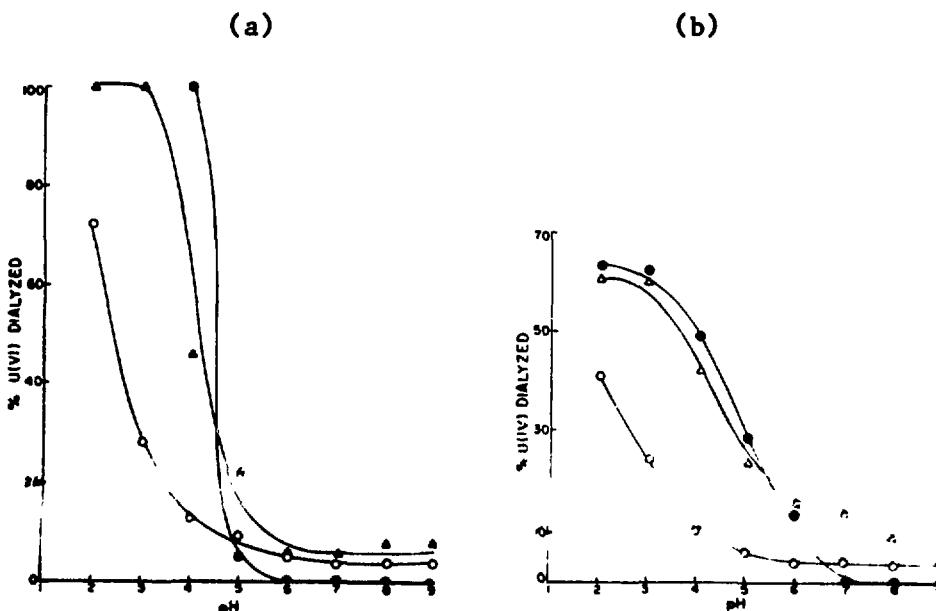
Fig. 17. Dialysis of an Aqueous Solution of Uranium as a
Function of pH in: o humic acid, △ fulvic acid,
● tannic acid. (a) U(VI) in 0.01M KNO₃. (b)
U(IV) in 0.01M NaCl. Copyright 1980 American
Chemical Society. Reprinted by permission [LI].

Li et al. [LI] studied the effect of U(VI) and U(IV) concentration
on the interaction of U(VI) and U(IV) with humic, fulvic, and tannic acids by
preparing solutions of 20 mg/L humic, fulvic, or tannic acid to which were
added various amounts of a standard solution of U(VI) and U(IV). The pH of
the systems was adjusted to 6.0. The systems were equilibrated for 48 hours
using dialysis bags containing 10 mL of ultrapure water. The results of these
experiments are summarized in Fig. 18. Figure 18(a) shows that, in experi-
ments with each of the three organic acids, the amount of free U(VI) ions
increases only slightly with increasing total U(VI) concentration at very low
ranges of concentration, but increases essentially linearly at concentrations
exceeding 5 to 10 µg/mL (i.e., organic complexing becomes less important with
increasing U(VI) concentration.) Figure 18(b) indicates a similar trend for
U(IV), although the linear increase in free U(IV) ions with increasing con-
centration begins at concentrations of only 1 to 2 µg/mL of U(IV).

(a)   (b)
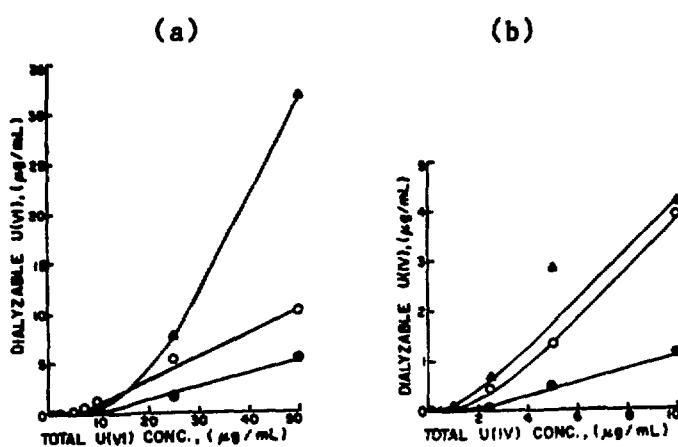
Fig. 18.   Dialyzable Uranium Concentration
           as a Function of Total Uranium
           Concentration at pH 6.0 in an
           Aqueous Solution Containing
           20 mg/L of: o humic acid,
           Δ fulvic acid, ● tannic acid.
           (a) U(VI).   (b) U(IV).   Copy-
           right 1980 American Chemical
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           sion [LI].

Li et al. [LI] used the results of these experiments to determine
the stability constants and the number of binding sites per unit weight of
organic ligand. Their data indicate that there are two binding sites on all
three ligands, one "strong" and one "weak," as shown by the stability constants
in Table 14. The two different binding sites make a difference of about two
orders of magnitude in the stability constants. The order of stability con-
stants for U(VI) is: FA > HA > TA and for U(IV) is HA > TA > FA. The order
of the number of binding sites is TA > HA > FA. The stability constants for
HA and TA complexed with U(IV) are larger than for U(VI), whereas the stability
constants for FA complexed with U(IV) are smaller than for U(VI). The number
of binding sites on these organic ligands for U(IV) is about half the number

Table 14. Stability Constants for Uranium-Organic
Complexes. Copyright 1980 American
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permission [LI].

Uranium Ion	Ligand	K_i	n_i, mmol/g
uranium(VI)	HA	5.4×10^6	1.0
		5.3×10^4	9.5
uranium(VI)	FA	2.7×10^7	0.2
		3.6×10^5	3.8
uranium(VI)	TA	2.3×10^6	0.6
		9.2×10^4	11.4
uranium(IV)	HA	9.5×10^6	0.5
		3.2×10^4	4.5
uranium(IV)	FA	4.4×10^6	0.3
		8.8×10^4	1.8
uranium(IV)	TA	8.5×10^6	0.9
		1.1×10^5	4.5

for U(VI). Li et al. interpret this fact to mean that U(VI) exists in solu-
tion as UO_2^{2+} (divalent) and U(IV) as U^{4+} (tetravalent); hence, 1:1 complexes
of organic ligands are formed with UO_2^{2+}, whereas 1:2 complexes are formed
with U^{4+}.

The formation of soluble chemical complexes is considered to be the
most common metal-organic interaction; however, some studies have suggested
that metal-organic interactions possess both the qualities of chelation and
colloid formation. At low metal concentrations natural organic substances
presumably remain in true solution, but at higher concentrations of metal
ions the organic substances and metals may associate to form larger particles
of colloidal dimensions that can precipitate or be removed by filtering through
a 0.45-μm filter. Means [MEANS-1982B] performed a series of flocculation
experiments with different metal ions (Na, Ca, Al, Fe(II), Fe(III), U, Th,
Np, Am, Pu) to examine the colloid-forming behavior of these ions with HA and
FA. The concentrations of the metal ions used in the experiments were (in
ppm): Na (900-1000), Ca (50-500), Al (10), Fe(II) (40-50), Fe(III) (10-50),
U(IV) (40-50), Th(IV) (10-50), ^{237}Np (4.7), ^{241}Am (1.02), and ^{239}Pu, presum-
ably present as PuO_2^{2+}, (0.54-5.4). Two different HA and FA concentrations
were used: 36-51 ppm and 5.1-7.8 ppm. The results of the experiments are
summarized below:

(1) The value of pH had little effect on blank HA and FA solutions
(i.e., no metal ions added). About 9% FA and 15% HA were
removed by flocculation at pH 3.8-4.0; however, flocculation
at higher pH values was practically negligible for both FA
and HA.

(2) All the metals tested caused some flocculation of HA and FA
and, in general, HA was flocculated to a greater extent than
FA by all metals tested. The metals Na and Ca had the least
influence on flocculation and Al and Fe had generally strong
effects.

(3) The solubility of the actinides (ability to remain in solution rather than to precipitate along with HA and FA colloids) varied with the actinide and the pH. Concentrations of Np in solutions containing 40-50 ppm HA or FA varied only slightly from those of blanks that contained no organic matter, although Np was slightly more soluble in the HA and FA solutions at pH 3.7-3.8 and 8.2-8.5 than in the blanks--suggesting formation of some soluble complexes of Np-HA or Np-FA. The Np caused flocculation of HA and FA but apparently remained soluble and did not precipitate along with the HA and FA. The metals Th and Am displayed enhanced solubility relative to blanks in the neutral to slightly basic pH range; however, in the low pH range, Th and Am precipitated along with flocculating HA and FA. Thus, Th and Am concentrations at low pH in the solutions containing organic matter are actually less than those in corresponding blank solutions. Little or no precipitation of U was shown at low pH relative to blanks, and enhanced solubility was shown at neutral to slightly basic pH. Enhanced solubility of Pu relative to blank solutions in all the solutions containing HA or FA was shown. The precipitation of HA and FA is promoted by Pu at pH 4, and some of the Pu presumably precipitates along with the organic matter as insoluble complexes; however, the soluble HA and FA form soluble complexes with a proportion of the Pu, to increase its solubility relative to blanks.

(4) The concentrations of HA and FA had little effect on the portion of HA or FA flocculated by a given metal; that is, low concentrations of these acids, more typical of ambient levels in natural waters, were flocculated to a similar extent as were high concentrations. Flocculation at higher HA and FA concentrations was more dependent upon pH, with increasing flocculation occurring with decreasing pH. The pH value was less important at lower HA and FA concentrations.

(5) For experiments run at two different metal concentrations, the removal of organic matter increased with increasing metal content.

We can conclude from Means' experiments that some insoluble actinide-organic complexes (colloids) formed under the conditions of high metal ion concentrations used in the experiments, but most of the actinides remained in solution. The presence of the actinides clearly caused flocculation of some of the HA and FA; however, in general, the actinide elements formed soluble complexes with remaining HA and FA, particularly at alkaline pH. These results are in contrast to the suggestion by other workers that insoluble complexes would most likely form under conditions of high metal ion concentration.

In a series of papers published between 1978 and 1981, Choppin and coworkers at Florida State University investigated the interaction of FA and/or HA with Am(III), Eu(III), Th(IV), UO_2^{2+} (uranyl), and radioactive calcium (^{45}Ca). To better understand the type and number of active complexing groups in HA, Choppin and Kullberg [CHOPPIN-1978] determined the pK_a and

enthalpy of protonation (addition of H^+ ions) of HA by pH and calorimetric titration. The value of pK_a was determined from the relationship

$$pK_a = pH - \log \frac{a}{1-a} \qquad (33)$$

where a is the degree of dissociation, as calculated from titration data. Plotting pK versus a and extrapolating to a = 0 gives the dissociation constant of the polymer at zero ionization (pK_0). Figure 19 shows the presence of two acidic groups with pK_a values of about 4.0 and 9.0. The pK_0 of the stronger acid (~4.0) was considered by Choppin and Kullberg to indicate a carboxylic functional group, possibly benzoate or salicylate. The weaker acid group was about 75% less abundant than the stronger group and is probably phenolic.

Fig. 19.

Plot of Apparent pK_a Values as a Function of Degree of Dissociation. Copyright 1978 Pergamon Press. Reprinted by permission [CHOPPIN-1978].
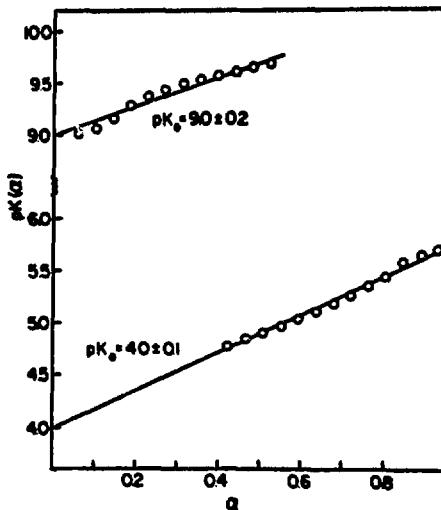
Choppin and Kullberg also examined the heat change (ΔH) on protonation of the humates as a function of pH (Fig. 20). The ΔH values were calculated per mole of H^+ exchanged. Their experiments showed that protonation reactions are fast, particularly within the basic region, and the shapes of the heat curves support the assumption that two types of functional groups are present in HA.

Bertha and Choppin [BERTHA] measured the binding constants (stability constants) of Eu(III) and Am(III) with HA and FA at a fixed pH (4.0) and ionic strength (I = 0.10) using a batch equilibrium technique. A stock solution of 0.09M KCl + 0.010M $NaC_2H_3O_2$, to which various concentrations of HA and FA were added, was spiked with ^{241}Am(III) and ^{152}Eu(III); 5 mL of this solution was added to a polyethylene vial containing 1 g of Dowex 50x8 resin and allowed to equilibrate for 60 hours on a rotating wheel. Duplicate aliquots of the equilibrated solution were withdrawn, filtered, and counted for gamma ray activity on a well scintillation counter.
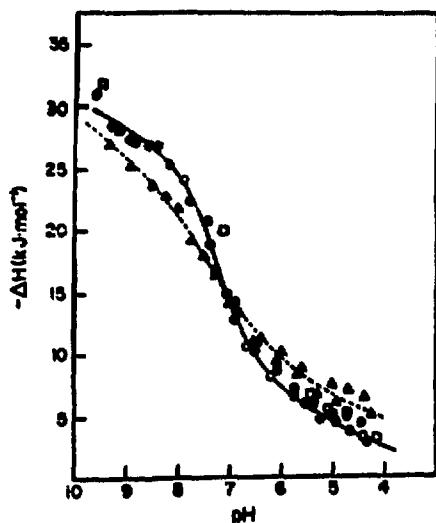
Fig. 20.

Variation of the Enthalpy of Protonation as a Function of the pH of the Measurement. The symbols indicate samples of humic acid from different sources. Copyright 1978 Pergamon Press. Reprinted by permission [CHOPPIN-1978].

The generalized reaction of a metal ion with fulvate or humate ions can be written as:

$$M + mX = MXm \tag{34}$$

$$B = (MXm)/\left((M)(X)^m\right) \tag{35}$$

where M refers to metal ions, X represents fulvate or humate anions, m is an integer number, and B is the binding constant or stability constant.

Distribution coefficients can be calculated from the relationship

$$\lambda = \frac{(M)resin}{(M)aq + (MXm)} \tag{36}$$

Figure 21 shows a pronounced linear trend of decreasing distribution coefficients for Am(III) and Eu(III) with increasing ligand concentration, indicating that these elements are strongly complexed by HA and FA.

Observing that the ratio of bound to free metal increased more rapidly than the concentrations of HA and FA, Bertha and Choppin [BERTHA] interpreted the results of their experiments to indicate the binding of Am(III) and Eu(III) to two types of sites with 1:1 and 1:2 stoichiometry. Marinsky [MARINSKY] disagrees with this interpretation. He suggests that the effects observed by these authors arises out of the tendency of HA and FA to aggregate and form separate phases, and does not indicate that they are associated simultaneously in 1:1 and 1:2 complexes. Bertha and Choppin's calculated binding constants for Am(III) and Eu(III) with FA and HA are shown in Table 15. In this table, β_1 values appear to refer to the binding constants of the 1:1 complexes and β_2 values to binding constants of the 1:2 complexes; the superscript (a) indicates values obtained after a correction factor was applied. Bertha and Choppin suggest that the enhanced binding

Fig. 21.

riation of the Distribution Coef-
cient (λ) with Humic and Fulvic
id Concentration. Each point
the average of 2-4 data. □ is
(III) and humic acid at 0.1°C;
is Eu(III) and fulvic acid at
°C. Copyright 1978 Pergamon
ess. Reprinted by permission
ERTHA].
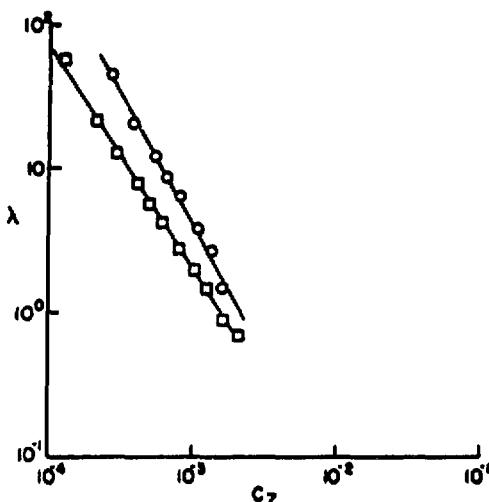
Table 15. Binding Constants for Eu(III) and Am(III) with
Fulvic and Humic Acids at pH 4.5. Copyright
1978 Pergamon Press. Reprinted by permission
[BERTHA].

	$\beta_1 (\times 10^{-6})$	$\beta_1{}^a (\times 10^{-6})$	$\beta_2 (\times 10^{-10})$	$\beta_2{}^a (\times 10^{-10})$
		Fulvic Acid		
Eu^b	1.8±1.3	3.1±2.2	1.95±0.29	3.28±0.49
		Humic Acid		
Eu^b	14.2±1.7	23.9±2.9	1.07±0.13	1.80±0.22
Am^b	4.1±1.2	6.7±2.0	2.29±0.10	3.78±0.17
Am^c	8.7±1.2	14.3±2.0	1.31±0.15	2.16±0.25

^{a}Values obtained after application of a correction factor.
^{b}25.0°C.
^{c}1.0°C.

) of Eu(III) by HA relative to FA is consistent with the relative values of
ι of the two polyelectrolytes, which are 4.65 for HA and 3.88 for FA. The
ιeral conclusion that Bertha and Choppin draw from this research is that the
ιvalent actinides would be strongly held by humic materials. In a later
ιer, Choppin [CHOPPIN-1980] published an expanded list of binding constants
:h HA (Table 16), which also included values for Th(IV) and $UO_2{}^{2+}$. The
.umn headed by α in this table indicates the degree of ionization of HA.

Nash and Choppin [NASH-1980] studied the binding of Th(IV) to HA and
Cation exchange capacity and degree of ionization as a function of pH were
:ermined by titration, and stability constants (Table 17) were measured by a
vent extraction method; note that HA-Th binding constants have higher values
m do FA-Th binding constants. Nash and Choppin interpret their data to
icate two types of thorium binding sites in the humic polymer containing

Table 16. Binding Constants of Selected Radionuclides
with Humic Acid. [CHOPPIN-1980].

Binding constants with humate $\mu = 0.10\underline{M}$; T = 25.0°C

Cation		α	log β_1	log β_2
Eu (III)	(3)	0.40[a]	7.78 ± 0.04	10.70 ± 0.05
Am (III)	(3)	0.40[a]	7.26 ± 0.11	11.04 ± 0.02
Th (IV)	(4)	0.25[a]	11.14 ± 0.01	16.17 ± 0.02
Th (IV)	(4)	0.43[a]	12.03 ± 0.02	17.29 ± 0.04
Th (IV)	(4)	0.54[a]	13.18 ± 0.04	18.43 ± 0.17
Th (IV)	(4)	0.37[b]	10.74 ± 0.01	15.79 ± 0.04
Th (IV)	(4)	0.39[c]	10.94 ± 0.02	16.43 ± 0.06
UO_2^{+2}	(5)	0.48[c]	7.28 ± 0.03	10.69 ± 0.04
UO_2^{+2}	(5)	0.67[c]	8.20 ± 0.03	11.55 ± 0.04

[a]Humic acid from a lake.

[b]Soil humic acid.

[c]Humic acid from Aldrich Chem. Co.

Table 17. Binding Constants for Th(IV) to Humic and Fulvic Acids.
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[NASH-1980].

log β_1	log β_2	T(°C)	pH	α	Material
11.140 (±0.013)	16.168 (±0.023)	25.0 (±0.5)	3.95	0.25	HA
12.027 (±0.023)	17.289 (±0.043)	25.0 (±0.5)	4.60	0.431	HA
13.181 (±0.038)	18.434 (±0.173)	25.0 (±0.5)	5.03	0.54	HA
11.534 (±0.024)	16.746 (±0.054)	50.0 (±0.1)	4.04	0.30	HA
10.680 (±0.100)	15.635 (±0.149)	5.0 (±0.1)	4.02	0.24	HA
10.738 (±0.010)	15.789 (±0.040)	25.0 (±0.5)	3.99	0.37	HA
10.940 (±0.019)	16.431 (±0.056)	25.0 (±0.5)	3.98	0.39	HA
9.798 (±0.029)	13.495 (±0.056)	25.0 (±0.5)	4.01	0.70	FA
10.824 (±0.051)	15.073 (±0.084)	25.0 (±0.5)	5.00	0.84	FA
9.528 (±0.044)	12.838 (±0.078)	4.3 (±0.1)	3.98	0.68	FA
10.023 (±0.021)	14.054 (±0.050)	52.0 (±0.1)	3.99	0.71	FA

one or two carboxylate groups. (In a later paper, these authors studied the
dissociation kinetics of Th and HA and concluded that Th(IV) is bound by at
least four types of sites with different basicities and different local polymer
structures [CHOPPIN-1981A].) They observed that complex stability is high and
that Th-humate binding constants increase with increasing ionization of the HA
and FA polyelectrolyte. Thermodynamic (entropy, enthalpy) data indicate that
the great stability of these complexes is derived from a very favorable com-
plexation entropy. Nash and Choppin conclude from their data that actinides

would be complexed completely by the humic materials in waters in the absence of other competing ligands such as carbonate and hydroxide. In soils, the binding by humate materials would be highly retentive to actinide migration.

Shanbhag and Choppin [SHANBHAG] and Choppin and Shanbhag [CHOPPIN-1981B] examined the binding of tracer level UO_2^{2+}(uranyl) and radiotracer ^{45}Ca to HA as measured by a solvent extraction technique. The binding of uranyl was interpreted as involving only the carboxyl groups of the humate, and both 1:1 and 1:2 ratios of $UO_2^{2+}:CO_2^-$ were observed. They suggest that uranyl binding by humic and/or fulvic materials is not significant in seawater because of competition from carbonate complexes, but may play a role in fresh-water systems where lower pH values prevail. Retention of uranyl from ground-water by soil humic substances would be strong. The uranyl interaction with humic substances is particularly interesting because UO_2^{2+} is a close chemical analog of PuO_2^{2+} but is more resistant to reduction; therefore, the behavior of uranyl is a valid model for that of PuO_2^{2+} in the absence of reduction of the Pu upon interaction with humate. Binding of ^{45}Ca by HA was found to be pH dependent. For an ionic medium of $0.1M$ $NaClO_4$, the binding constant ranged from 2.25 ± 0.04 at pH 3.9 to 3.32 ± 0.04 at pH 5.0. Thermodynamic parameters of binding calculated from the temperature coefficient indicated that a large, positive entropy change accounts for the favorable free energy of complexation.

Complexing of Eu(III) by FA was studied in detail by Marinsky [MARINSKY], using potentiometric titration. He determined that FA at concentration levels as low as $10^{-4}M$ (~20 ppm), on a monomer basis, exists in aqueous media as small molecular aggregates that exhibit microgel properties. This conclus'on was based upon two principal observations. (1) In studies of the distribution of ^{154}Eu between 8% Dowex 50 resin in the Na^+-ion form and FA at several different concentration levels, and over an extended pH range from 4 to 10, it was shown that only one FA-complexed species of Eu(III), $[Eu(COOR)]_n^{++}$, was formed; its apparent constant of formation, $\beta_{Eu(COOR)^{++}}$, is roughly proportional to the third power of the NaCl concentration used in the study. (2) An inverse relationship exists between apparent pK_a and ionic strength. At low ionic strength the apparent pK_a is higher than at high ionic strength. Marinsky also noted that pK_a was lowered by increasing the FA concentration. This decrease in pK_a appears to indicate the formation of a more compact aggregate. The capacity of the samples studied by Marinsky varied from sample to sample and the capacity was also shown to decrease with time.

Marinsky [MARINSKY] examined the effects of FA concentration on binding with Eu(III) at an ionic strength of 0.1 and a wide range of pH values. He observed a 25-fold increase in the ratio of bound to free Eu(III) when the concentration of FA was increased by only a factor of five. At an ionic strength of 0.3, the change of the ratio of bound to free Eu(III) for a similar fivefold increase in FA concentration was much smaller, about a two-fold increase. This observed behavior is attributed to the existence of FA as a flexible microgel that forms as a result of the strong tendency for FA molecules to aggregate. At the lower ionic strength of 0.1, the aggregate arrangement apparently becomes more compact as the concentration of FA increases because cohesive forces originating in the polar sites of the FA molecule are enhanced by the higher concentration of these sites. At the higher ionic strength of 0.3, an even more compact assembly of FA molecules becomes

somewhat less compact with increasing concentration of FA because repulsive forces originating in the positive charge on the partially dissociated molecule become slightly disruptive. Because of the closer approach of neighbor molecules owing to the more compact arrangement of the FA microgel, an increase in FA concentration apparently leads to a slight expansion of the microgel because of such repulsion.

Ionic strength also affects the ratio of bound to free Eu(III), as shown in Fig. 22. Binding of Eu(III) with FA increases as ionic strength decreases. This behavior is apparently due to the fact that FA exists as a gel whose solvent uptake results in a counterion concentration of $\sim$0.2$\underline{M}$. In the most dilute salt systems, the ratio of bound to free Eu(III) measured is extremely large because of the fact that the concentration of free Eu(III) ions, to which the quantity of bound Eu should be related, is so much larger than that observed in the aqueous phase. Note in Fig. 22 that the ratio of bound to free Eu(III) increases sharply with increasing pH at pH values below $\sim$6, but reaches a plateau between pH values of about 6 and 8. This plateau is thought to coincide with the pH range in which the availability of carboxylic acid groups of the FA has reached its maximum value. This behavior suggests that the complexed species of Eu(III) is exclusively associated with the carboxylic acid constitutents of the FA. The gentle increase in the binding ratios with increasing pH beyond the carboxylic acid equivalence point may signal the binding of another functional unit of FA, e.g., phenol, or may be just a reflection of gel phase contraction in this pH range. The somewhat anomalous binding behavior in the 0.30$\underline{M}$ solution, which shows an early plateau that persists over the pH range of $\sim$6 to $\sim$10 (Fig. 22), may be caused by the FA aggregate expanding over this pH range in this higher ionic strength system.

Marinsky [MARINSKY] also examined the competitive complexing of Eu(III) by FA and CO_3^{2-} ion. He concluded that, at a pH of 8, Eu(III) can be expected to be complexed more strongly than CO_3^{2-} by as little as 2 ppm of FA when the HCO_3^- concentration does not exceed 250 ppm.

D.   Discussion: Factors Affecting Radionuclide-Organic Complexing

The review in Sections IV.A, B, and C serves to illustrate major trends of research in the field of radionuclide-organic complexing, as well as some of the problems that still face researchers in understanding organic complexing. Although it is quite clear from published research results that humic substances can form stable complexes with a variety of radionuclides under laboratory conditions, the effects of complexing on the mobility of radionuclides in the soil and groundwater environment are less clear. If these stable complexes are soluble, radionuclide mobility can apparently be increased; however, insoluble complexes may also form that can either precipitate or bind chemically to soil particles, causing decreased mobility of the nuclides. One of the goals of future research must be to investigate more thoroughly the relative importance of soluble and insoluble radionuclide-organic complexes in natural systems. It is particularly important that we develop a better understanding of the factors that control the formation of soluble and insoluble radionuclide-organic complexes in groundwater aquifers that may be subject to contamination by high-level radioactive waste from deep repositories.
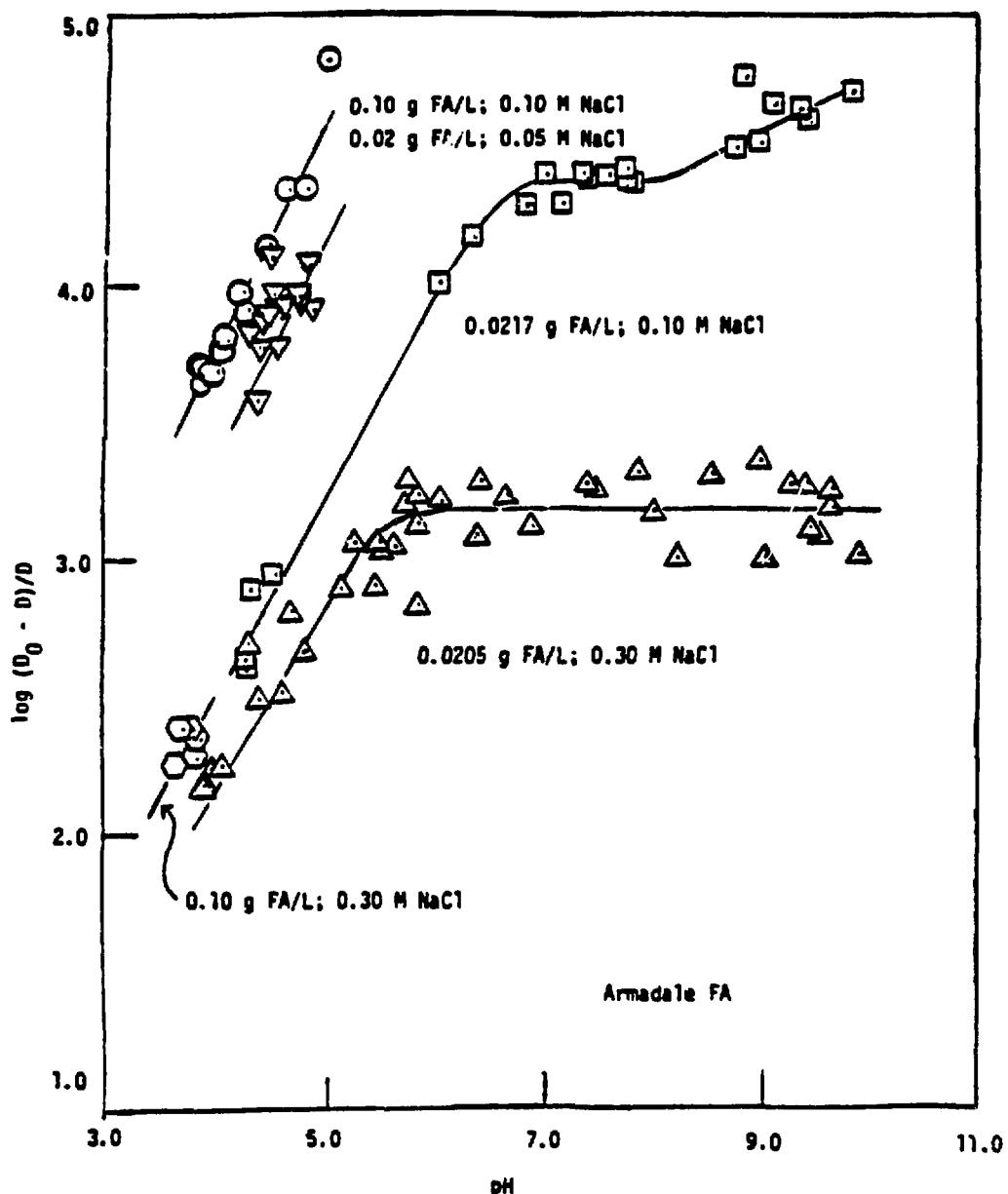
Fig. 22. Dependence of the Logarithmic Ratio of Bound to Free
^{154}Eu(III) on pH. Other variables: fulvic acid
concentration, ionic strength. Copyright 1983
SKBF/KBS. Reprinted by permission [MARINSKY].

Several important factors are known to influence the solubility of
radionuclides and trace metals. These factors include the oxidation state,
pH, temperature, ionic strength of the solutions, metal or radionuclide con-
centration, and concentration of dissolved humic substances (HA and FA). The
effects of these variables on complexing of trace metals by humic substances

are discussed in Section III. Considerable work has also been done to evaluate the effects of oxidation state, pH, temperature, ionic strength, and radionuclide concentration on the solubility of ionic species and inorganic complexes of radionuclides in solutions containing little or no DOC. Much less research has been done to study the effects of these variables on the solubility of radionuclide-organic complexes; however, enough work has now been done to provide some general insight into differences in behavior of radionuclides in aqueous systems that contain dissolved organic substances and in those that do not. The effects of environmental variables and radionuclide/DOC concentrations on radionuclide-organic complexing are examined in greater detail in this section.

1.   Oxidation State of Actinide Elements

Oxidation state is generally considered to be one of the most important controls on radionuclide mobility. Many of the actinides exist in multiple oxidation states (Table 18); the most common oxidation states are represented by the M^{3+}, M^{4+}, MO_2^+(V), and MO_2^{2+}(VI) species. The oxidation-reduction behavior of U, Np, and Pu is particularly complicated, and multiple oxidation states can coexist in solution [WATTERS-1980]. The oxidation states of importance for actinides under environmental conditions are likely to be Am(III), U(IV), U(VI), Np(IV), Np(V), Pu(IV), and Pu(V) [BONDIETTI-1980 -1981]. The stable oxidation state in the environment will be governed by the presence of oxidizing and reducing agents and complexing ligands. Wahlgren et al. [WAHLGREN-1976] suggest that, because of similar electronic structure and ionic radii, transuranic elements of a given oxidation state should behave in a similar manner chemically. Thus, the behaviors of Pu(III) and Am(III) are similar, as are those of Pu(IV) and Th(IV), and Pu(VI) and U(VI). In general, the actinides appear to be more soluble in their higher oxidation states than in their reduced forms [SERNE-1982]. For example, both U(IV) and Th(IV) are extremely resistant to leaching; however, oxidation of U(IV) to U(V) results in much higher mobilization [BONDIETTI-1980].

Table 18.   Comparison of Oxidation States for the Actinide Elements in Solution.[a] [WATTERS-1980].

f = 1	2	3	4	5	6	7	8	9	10
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
						2			2
3		3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4		
		5	5	5	5	5			
			6	6	6	6			
				7	7				

[a]The solid lines bound the most likely oxidation states in aqueous solution.

In the case of Pu, all oxidation states can exist in aqueous solutions under the Eh-pH conditions of environmental interest, and strong complexes are formed between Pu and oxygen-containing ligands (O^{2-}, OH^-, CO_3^{2-}, etc.) [ALLARD-1983]. The complex strength increases with the effective charge of the acceptor ion in the order: $Pu^{4+} > PuO_2^{2+} > Pu^{3+} > PuO_2^+$. As is the normal pattern for polyvalent ions, lower oxidation states of Pu are stabilized by more acidic conditions, whereas higher oxidation states become more stable as the basicity increases [CHOPPIN-1983].

The presence of dissolved humic substances in aqueous systems appears to have two opposing effects on the actinides. On the one hand, the presence of HA or FA can bring about reduction of actinides, such as Pu(V) to Pu(IV), causing a decrease in solubility and mobility; however, competitive chelation may act in the opposite direction to increase mobility [DAHLMAN]. The formation of complexes can affect oxidation-reduction potentials and stabilize different oxidation states in solution, depending upon relative values of stability constants. The general order of stability constants is $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$ [WATTERS-1980]. Dahlman et al. [DAHLMAN] suggest that the tendency of the actinides to form complexes with organic ligands follows the order: $Pu(IV) > Th(IV) > Am(III) = Cm(III) \overset{\sim}{=} U(VI) > Pu(VI) > Np(V)$.

Bondietti et al. [BONDIETTI-1975] experimentally investigated the redox behavior of Pu in the presence of HA and FA. Reduction of Pu(VI) and Pu(V) to Pu(IV) occurred readily. The most stable valence upon reaction with these humic substances was Pu(IV) and is therefore likely to be the predominant oxidation state in most environments where humic substances are moderately abundant. Further reduction of Pu(IV) to Pu(III) also occurred; however, reduction from the tetravalent to the trivalent state took place only at low values of pH (<3.1) under aerobic conditions. Reduction could also occur at higher pH values under anaerobic conditions, but probably not above pH 6 owing to the stablizing effect of strong hydroxide complexes formed in the tetravalent state.

Because of the lower solubility of Pu(IV) compared to Pu(V) or Pu(VI), Pu should be relatively immobile in environmental systems; however, Bondietti et al. [BONDIETTI-1975] point out that, if Pu(IV) is the predominant valence that stabilizes in soils and other environmental matrices, the chemistry of Pu in the environment will be strongly affected by complex formation. Inorganic complexers such as hydroxides may be very significant, but organic complexers may be more important in maintaining Pu(IV) in forms that are mobile in the environment, i.e., complexed forms. On the other hand, Bondietti et al. demonstrated that much of the Pu in soils contaminated by fallout 30 years previously was complexed to insoluble humic substances that were bound to soil particles, resulting in very low mobility of the Pu.

Nash et al. [NASH-1981] studied the reducing effects of HA on hexavalent actinides. It strongly absorbs U(VI), Np(VI), and Pu(VI) from aqueous bicarbonate-carbonate media. The HA also reduced Np(VI) to Np(V) and Pu(VI) to Pu(V); however, it did not reduce U(VI). It complexed both the (IV) and (VI) valence states of Pu and Np strongly enough to prevent carbonate complexes. Complexes between NpO_2^+ and HA occur at neutral to alkaline pH. The mobility

of the actinides in the (IV), (V), and (VI) oxidation states will thus be governed by the mobility of HA. Nash et al. suggest that, because HA can be strongly bound to clays, their research results imply probable low mobility of the actinides in waters contacting humic materials. This conclusion does not necessarily apply, however, if the HA forms soluble complexes with the actinides.

Nelson et al. [NELSON-1980] found that the Pu in many oligotrophic lakes is primarily in the oxidized form [presumably Pu(V)], which is weakly sorbed onto particulates in the water. Some reduced Pu, presumably Pu(IV), was also found in all the waters. The Pu(IV) formed strong, soluble complexes with the dissolved indigenous organic substances in the lake waters, inhibiting sorption of the Pu onto particulates. The solubility of the complexes varied directly (increased) with increasing concentration of DOC.

2. Effects of pH

The complexing of actinides with HA and FA is strongly dependent upon pH because both the hydrolysis of the nuclides and the dissociation of the acids are pH dependent [OLOFFSON]. The pH also affects the oxidation state of polyvalent cations. In general, lower oxidation states are stabilized by more acidic conditions, whereas higher oxidation states become more stable as the basicity increases [CHOPPIN-1983]. Choppin points out, however, that this general trend can be negated by other factors, such as complexing, that can even reverse the trends and the relative stability of the different oxidation states.

Li et al. [LI] determined that complexation of U(VI) and U(IV) with HA, FA, and TA was pH dependent. Complexation increased with increasing pH, with particularly strong enhancement taking place at pH values above about 5, as shown in Fig. 17, which also shows that HA can complex with both U(IV) and U(VI) at lower pH values than FA. Shchebetkovskii and Bochkov [SHCHEBETKOVSKII] studied the absorption of Pu by humic substances as a function of pH. They observed that sorption onto the humic substances, measured by distribution coefficients (K_d), increased linearly within the pH range of $\sim 0.5-1.5$ with increasing pH according to the equation,

$$\log K_d = (a)pH + b \tag{37}$$

where a and b are constants. These pH values are, of course, well below those that could be expected under most environmental conditions.

Flocculation studies by Means [MEANS-1982B] demonstrate that Am, Np, Th, and Pu solubilities are affected by the presence of HA and FA and by pH. In HA and FA solutions at both low pH (3.7-3.8) and high pH (8.2-8.5), Np was found to be only slightly more soluble than in blank solutions containing no HA or FA. Although Th and Am displayed enhanced solubility in neutral to basic HA and FA solutions, they flocculated or precipitated in the low pH range, indicating that their solubility at low pH is actually lower in HA and FA solutions than in blank solutions. Enhanced solubility was shown by U at neutral to basic pH compared with low pH; Pu was more soluble in all the solutions containing HA and FA than in blank solutions.

Cleveland and Rees [CLEVELAND-1976] found little solubilization of Pu and Am in soil suspensions at pH values ranging from 6.5 to 7.5, but solubilization increased (though only slightly) at a pH of 9. Nishita and Haug [NISHITA] observed that pH has a marked influence on extractability (solubility) of Pu in HA and FA solutions. Extractability is at a maximum at pH 1.2, drops to about 40% at pH 3.3, remains constant between pH 3.3 and 7.2, increases abruptly between pH 7 and 10.7, and decreases sharply above pH 10.7.

All these reported studies indicate a general trend of increasing solubilization (decreasing sorption) of actinides with increasing pH in the presence of HA and FA, although the trend is by no means linear. Thus, in general, neutral to basic pH values favor solubilization over acidic pH values. (Note that HA becomes insoluble at acid pH values, particularly below pH 4.) This trend appears to be opposite to that apparently found in most studies in which the sorption of radionuclides to rock materials has been examined in solutions free of humic or other organic substances. These adsorption studies typically show that nuclide adsorption onto solid phases increases (solubility decreases) as pH increases [SERNE], although this trend may not hold throughout the entire range of pH values. Allard and Beall [ALLARD-1979] have shown, for example, that sorption of Am increases with increasing pH in the range of 4 to about 6.5, but decreases slightly at higher pH. On the other hand, sorption of Np increases only slightly below pH 4 to 6.6, or decreases slightly depending upon the adsorbing solid, but increases sharply at higher pH. Thus, increasing pH appears to favor formation of soluble complexes of radionuclides in the presence of humic substances and decreased sorption onto solid phases, in contrast to increased sorption onto solid phases in the absence of humic substances. Because the pH of most deep groundwaters is likely to be basic (about 8-9), the presence of humic substances in these waters may be a critical factor in determining radionuclide mobility. Additional research on the effects of pH on the mobility of radionuclides in the presence of HA and FA is clearly needed.

3. Effects of Temperature on Radionuclide Mobility in the Presence of Organic Complexants

Relatively few studies have examined the effects of temperature on the mobility (solubilization) of radionuclides in the presence of organic complexants, although many studies have investigated the effects of temperature on sorption of radionuclides in organic-free solutions. Serne and Relyea [SERNE] summarize studies of radionuclide sorption performed under the Waste/Rock Interactions Technology (WRIT) program and report that, in general, these studies show sorption of most radionuclides is not significantly affected by temperature variations within the range of 20 to 80°C. Other published reports disagree with these conclusions. For example, Salter et al. [SALTER] report that temperature has a strong effect on sorption of several radionuclides onto Columbia River basalts. Sorption of many radionuclides, as measured by distribution ratios (K_d), increased with increasing temperature. Values of K_d for Ra, Am, Pu, and Se all increased between 25 and 60°C. On the other hand, the distribution coefficient for Cs decreased with increasing temperature, and Sr sorption was not affected between 25 and 60°C.

Means et al. [MEANS-1983] reported a significant relationship between temperature and sorption of U, Cs, Sr, and Co onto kaolinite, illite, and montmorillonite in the presence (and absence) of the organic complexants, oxalic acid and EDTA. Figure 23 shows the results obtained in experiments with oxalic acid. A general trend of increasing sorption (decreasing concentration of radionuclides in solution) with increasing temperature within the temperature range of 0 to 250°C is evident in runs both with and without organic complexants. Note, however, that considerable variation in sorption behavior of these radionuclides occurs. Some of the nuclides display reversals of this trend; that is, sorption decreases with increasing temperature within certain temperature ranges. For example, U adsorption on montmorillonite and illite generally increased to about 75°C in solutions without oxalic acid and then decreased; sorption of both Cs and Sr on kaolinite and montmorillonite first decreased and then increased. Nuclide sorption in the presence of oxalic acid showed the same general behavioral trends as in the absence of organic complexants; however, the presence of oxalic acid generally decreased sorption in all temperature ranges. Similar results were obtained in experiments with EDTA.

Boggs and Seitz [BOGGS-1984A] investigated the effects of temperature on sorption of Am and Np onto basalt in both humic-free solutions and solutions containing HA and FA ranging in concentration from 1 to 200 mg(C)/L. The results indicate a significant increase in sorption of Am and Np at 90°C in both HA and FA solutions compared with that at 22°C. The greatest effect on sorption was evident in solutions containing no HA or FA; the effects of temperature on sorption decreased slightly with increasing concentration of HA and FA in solution. Temperature effects appear to be interrelated with pH effects in a complicated way; that is, the smallest increases in sorption with increasing temperature were observed in experiments in which pH was adjusted to 9.0 at all concentration levels of HA and FA, in contrast to experiments in which pH was allowed to range from 8.8 to 9.9 depending upon the concentration of HA and FA in solution.

Too few experimental data are yet available to allow definite conclusions about the effects of temperature on the mobility of radionuclides in the presence of humic substances and other organic complexants. Preliminary data suggest a general trend of decreasing solubilization of many radionuclides (increasing sorption onto solid phases) with increasing temperature; however, the effects vary with different nuclides and within different temperature ranges. Increase in concentration of HA and FA and other organic complexants generally works to increase solubilization, thereby reducing the tendency of increased temperature to cause reduced radionuclide solubility. The effects of temperature changes in the presence of organic chelates vary with different radionuclides and within different temperature ranges. Means [MEANS-1983] reports that at temperatures of about 150 to 200°C organic complexants began to degrade and lose their metal-binding capabilities.

4. Effects of Ionic Strength

Serne and Relyea [SERNE] report that studies performed under the WRIT program generally show that nuclide adsorption for alkali and alkaline earth elements exhibits a consistent decrease in distribution ratios (decreased sorption) as the groundwater [Na⁺] or [Ca²⁺] increases. They indicate that
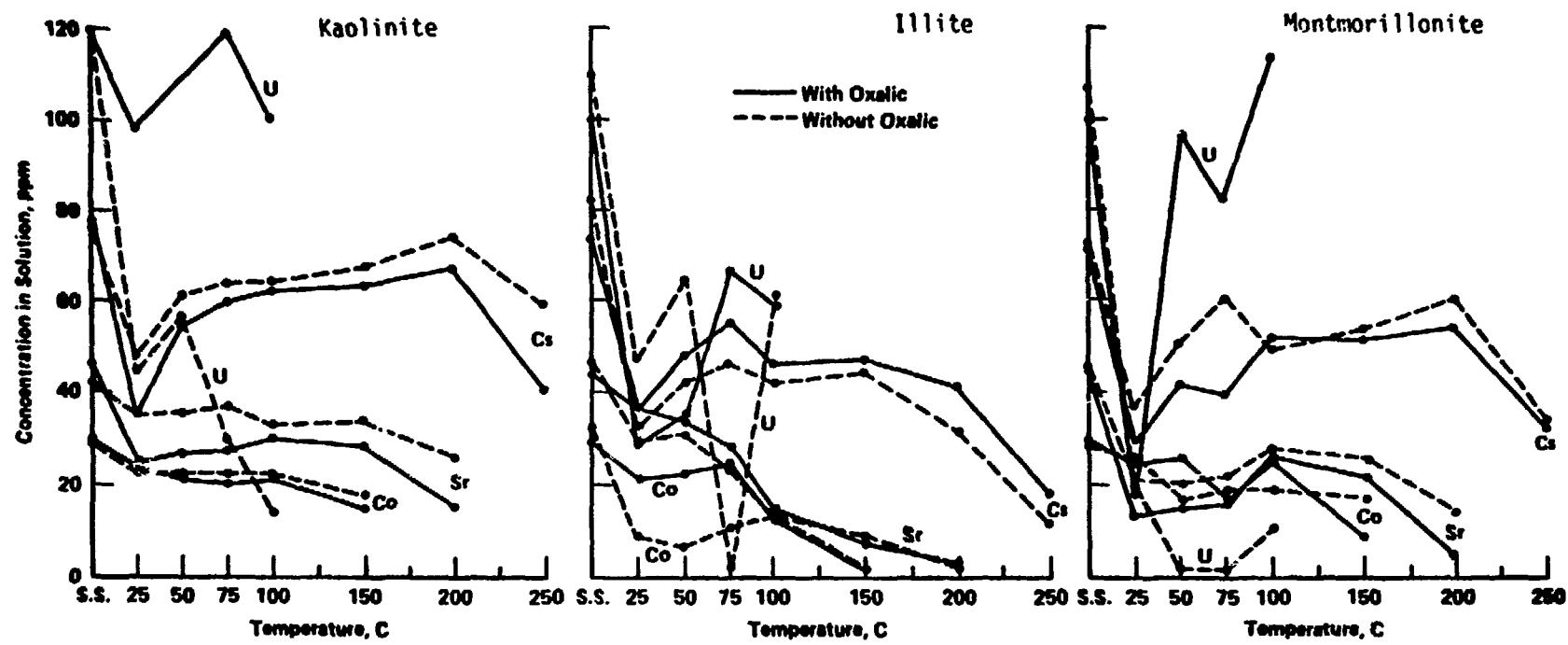
Fig. 23. Concentrations of U, Co, Sr, and Cs in Aqueous Systems Containing Kaolinite, Illite, and Montmorillonite, Both with and without Oxalic Acid, as a Function of Temperature. Run durations: kaolinite 0–75°C, 8 days; and 100–250°C, 8 days; illite 0–75°C, 9 days; and 100–250°C, 23 days; montmorillonite 0–75°C, 16 days; and 100–250°C, 12 days. [MEANS–1983].

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distribution ratios at neutral pH values for lanthanide elements such as Eu and for the actinides are much less sensitive to ionic strength. Actually, U and Np show increased adsorption in brines. Serne and Relyea conclude on the basis of the WRIT studies that, except for Sr, Cs, Ra, and a few other long-lived nuclides, ideal ion exchange processes are of limited utility in explaining nuclide retardation.

Most studies of metal-organic complexing discussed in Section III found that stability constants of the complexes decrease with increasing ionic strength, indicating that, in general, the stability of complexes formed between humic substances and divalent metals decreases with increasing ionic strength. For example, thermodynamic modeling studies by Stumm and Morgan [STUMM] suggest that metal-organic complexes in natural waters enriched in Ca and Mg may be relatively unimportant owing to the inhibiting effect on trace metal-organic complexing caused by high concentrations of Ca^{2+} and Mg^{2+}. Unfortunately, only a few studies have examined the effects of ionic strength on the stability of radionuclide-organic complexes. In one such study, Marinsky [MARINSKY] reported the effects of ionic strength on binding of Eu by FA. Experiments with solutions ranging in concentration from 0.05 to $0.30\underline{M}$ NaCl demonstrated an increase in binding (complexing) of Eu with decreasing ionic strength of the solutions, as shown in Fig. 22. As that figure shows, the magnitude of the decrease varies with pH. Preliminary studies thus suggest that the stability of radionuclide-organic complexes, like that of trace metal-organic complexes, decreases in the presence of increasing concentrations of competing cations; however, additional studies of the effects of overall ionic strength on the stability of specific radionuclide-organic complexes are needed to refine this conclusion.

5.   Effects of Competing Ligands

An additional problem related to ionic strength is the presence of inorganic ligands such as CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^-, and PO_4 in most natural waters. These inorganic ligands can form complexes with available metals ions, including radionuclides; therefore, competition with inorganic ligands must be considered when evaluating the stability of radionuclide-organic complexes. In the alkaline groundwaters environment, within which most high-level radioactive waste repositories will probably be sited, carbonates are the most likely inorganic ligands to interact with radionuclides.

Marinsky [MARINSKY] examined the possibility that carbonate ions could complex with ^{154}Eu (III) more strongly than FA in the pH range of 8 to 9. Complexation of Eu(III) by both CO_3^{2-} ion and FA was studied in a water sample containing 20 ppm FA organic carbon ($\sim 1.5 \times 10^{-4}M$) with 200 ppm of HCO_3^- ion ($3.3 \times 10^{-3}\underline{M}$) and either 50 or 550 ppm (10^{-3} or $10^{-2}\underline{M}$) NaCl. Marinsky reports that, at pH 8, the Eu(III) is more strongly complexed by FA (from three different sources) at both concentrations of NaCl examined. At pH 9, the preference of Eu(III) for FA relative to the CO_3^{2-} ion is reduced, so that the least strongly binding FA source is only slightly more strongly complexed than the CO_3^{2-} ion in the more dilute NaCl system. At the higher concentration of NaCl, Eu(III) is predicted to be four times more strongly bound to the carbonate ion than to the least strongly binding FA, but 3 to 20 times more strongly bound to the other FA sources than to the carbonate ion. Thus, it appears that the relative strengths of FA-Eu and CO_3^{2-}-Eu

complexes are functions of the source (type) of FA as well as pH and ionic strength. Marinsky concludes that, at a pH of 8, Eu(III) can be expected to be complexed more strongly by FA than by the CO_3^{2-} ion by as little as 2 ppm of FA when the HCO_3^- concentration does not exceed 250 ppm.

Mathew and Pillai [MATHEW] studied the complexing of Pu with carbonate ion in the presence of ~20 mg/L of organic matter in seawater containing up to 96 mg/L (10^{-3}M) carbonate/bicarbonate. Their results are shown in Table 19. They found that the Pu solubilized (complexed) is more or less directly proportional to the carbonate added, but that solubilization of Pu is much higher if organic matter is added to the sea water. Furthermore, the results indicate that the amount of Pu solubilized vs. the amount of organic matter increased with increase in carbonate/bicarbonate concentration. Thus, in this particular experiment at least, the complexing of Pu with organic matter appears to actually be enhanced by the presence of carbonate ion.

Table 19. Influence of Carbonate, Bicarbonate, and Organic Matter on Solubilization of Pu in Filtered Seawater. [MATHEW].

Experiment	Soluble plutonium		
	(dis/min per 100 mL)	(M)	(µg Pu/L)
Sea water with low $CO_3^=$, (3.6 mg/L) pH: 7.45	60	1.9×10^{-11}	4.4×10^{-3}
Sea water with low $CO_3^=$, HCO_3^- + 20 mg organic matter	180	5.6×10^{-11}	13.1×10^{-3}
Sea water with normal $CO_3^=$, HCO_3^- concentration (24.6 mg/L) pH: 7.9	72	2.2×10^{-11}	5.3×10^{-3}
Sea water with normal $CO_3^=$, HCO_3^- concentration + 20 mg organic matter	212	6.6×10^{-11}	15.5×10^{-3}
Sea water with excess $CO_3^=$, HCO_3^- (96.36 mg/L) pH: 8.2	141	4.4×10^{-11}	10.3×10^{-3}
Sea water with excess $CO_3^=$, HCO_3^- + 20 mg organic matter	512	15.9×10^{-11}	37.3×10^{-3}

Nash et al. [NASH-1981] investigated the reaction of hexavalent actinides with HA in aqueous carbonate and bicarbonate solutions. They report that HAs not only are effective reducing agents for hexavalent neptunium and plutonium, but also complex the (IV) and (VI) valence states strongly enough to prevent carbonate complexes. On the other hand, Wahlgren and Orlandini [WAHLGREN-1982] found that the high alkalinity in some North American lakes containing high DOC concentrations had little effect on Pu distribution coefficients, but caused a significant decrease in the distribution coefficients of U. They conclude that, when alkalinity is high and pH exceeds 7.5, alkalinity rather than DOC concentration appears to control the adsorption behavior of U.

6. Effects of Radionuclide Concentration

Serne and Relyea [SERNE] report that, in contrast to the traditional assumption that the nuclide isotherm is linear (i.e., the distribution ratio is constant with changes in nuclide concentration), WRIT studies found that adsorption of most nuclides (including Cs) exhibit nonlinear sorption isotherms for rock materials, even at extremely low nuclide concentration ranges ($10^{-9}\underline{M}$ and lower). For example, in these studies Seitz et al. [SEITZ] observed a pronounced increase in sorption of Cs onto limestone with decreasing concentration of Cs in solution within the concentration range of $\sim 10^{-10}$ to $10^{-2}\underline{M}$. A similar relationship of increasing distribution ratios with decreasing concentration of Cs within the concentration range of 10^{-7} to $10^{-3}\underline{M}$ was observed by Torstenfeld et al. [TORSTENFELD] in studies of Cs sorption on Stripa granite. When clay minerals or weathered rocks with high clay content are the sorbing materials, more of the nuclides approach linear isotherms; however, the majority continue to exhibit nonlinearity. Thus, the WRIT studies suggest that, in most cases, distribution ratios increase (sorption increases) as the nuclide concentration decreases.

Studies of metal-organic complexing reported in Section III suggest a general trend oi decreasing complexing ability with increasing metal ion concentration. This trend was reported by Kerndorff and Schnitzer [KERNDORFF] as well as Ong et al. [ONG]; however, other investigators (e.g., Saar and Weber [SAAR-1979]) have observed variations in this trend depending upon the metal ion being studied.

The general trend of decreasing complex stability with increasing metal ion concentration appears to hold also for radionuclide-organic complexing. Li et al. [LI] used dialysis techniques to examine the effects of U(VI) and U(IV) concentration on the interaction of these radionuclides with 20 mg/L HA, FA, or TA (Fig. 18). A strong relationship between nuclide concentration and the degree of nuclide-organic complexing was observed. A nearly linear decrease in complexing [increase in free U(VI) ion concentration] with increasing total U(VI) concentration at concentrations greater than about 5 to 10 mg[U(VI)]/L was established for all three organic complexants. A similar trend was observed for U(IV) at concentrations greater than about 1 to 2 mg/L. Means [MEANS-1982B] examined flocculation of Th, Am, U, and Pu in the presence of HA and FA at different nuclide concentrations. For experiments run at two different nuclide concentrations, Means determined that the removal of HA and FA by flocculation (of insoluble actinide-organic colloids)

increased with increasing metal content of the solutions. This behavior suggests that increase in nuclide concentration causes a decrease in soluble nuclide-organic complexation--the same trend observed by Li et al. [LI].

The decreasing tendency to form soluble radionuclide-organic complexes with increasing radionuclide concentration indicates that, if the concentration of HA or FA in a solution is held constant, further addition of the radionuclide to the solution will decrease the capacity of the solution to form soluble radionuclide-organic complexes. Reducing the capacity of a solution to form soluble complexes with a radionuclide has the practical effect of increasing sorption of the radionuclide onto rock materials. On the other hand, the adsorption studies reported by Serne and Reylea [SERNE], which were conducted in the absence of DOC, show that radionuclide sorption onto rock materials generally decreases (mobility of the radionuclide increases) as the concentration of the radionuclide in solution increases. Thus, in the presence of humic substances, the general tendency toward increased mobility of radionuclides caused by increased concentration of the radionuclides appears to be offset to some degree by the fact that increased nuclide concentration reduces soluble nuclide-organic complexes in the solution.

7. Effects of Dissolved Organic Carbon Concentration

Several investigators have studied the effects of DOC concentration on complexing of radionuclides by organic substances. Most studies have established a strong correlation between increasing solubilization (complexing) of radionuclides and increasing concentration of organic complexants. Nelson et al. [NELSON-1980] demonstrated that sorption of Pu onto suspended solids in lake waters varies inversely with the DOC content of the water within the approximate concentration range of 1 to 100 mg(C)/L. Wahlgren and Orlandini [WAHLGREN-1982] reported a similar, essentially linear relationship between sorption of Pu, Th, and U and DOC concentration in lake waters, and Orlandini [ORLANDINI] found the same inverse relationship between Am and DOC concentration in lakes. Marinsky [MARINSKY] observed a 25-fold increase in the ratio of bound (complexed) Eu(III) to free Eu(III) when the concentration of FA in experimental solutions was increased by only a factor of five.

Boggs and Seitz [BOGGS-1984A] studied the influence of different concentrations of HA and FA on sorption of Am and Np onto basalt. Batch partitioning experiments were carried out with synthetic groundwaters in which ionic strength and nuclide concentration were held constant. In one experiment, pH was maintained at a constant value of 9.2; in other experiments, pH ranged from 8.8 to 9.9 depending upon the concentration of HA or FA added to the groundwater. Temperature was maintained constant at either 22 or 90°C. Experiments were conducted with groundwaters containing 0, 1, 10, 20, 100, and 200 mg(C)/L of HA or FA. The solutions were spiked with Am or Np and allowed to equilibrate with crushed basalt for seven days. Distribution ratios were calculated based on the ratio of nuclide sorbed onto the basalt to nuclide remaining in solution at the end of the experiment.

The results of the experiment with HA and Am at a fixed pH of 9.2 are summarized in Fig. 24, which shows a very strong inverse relationship between distribution ratio (sorption) and the concentration of HA organic
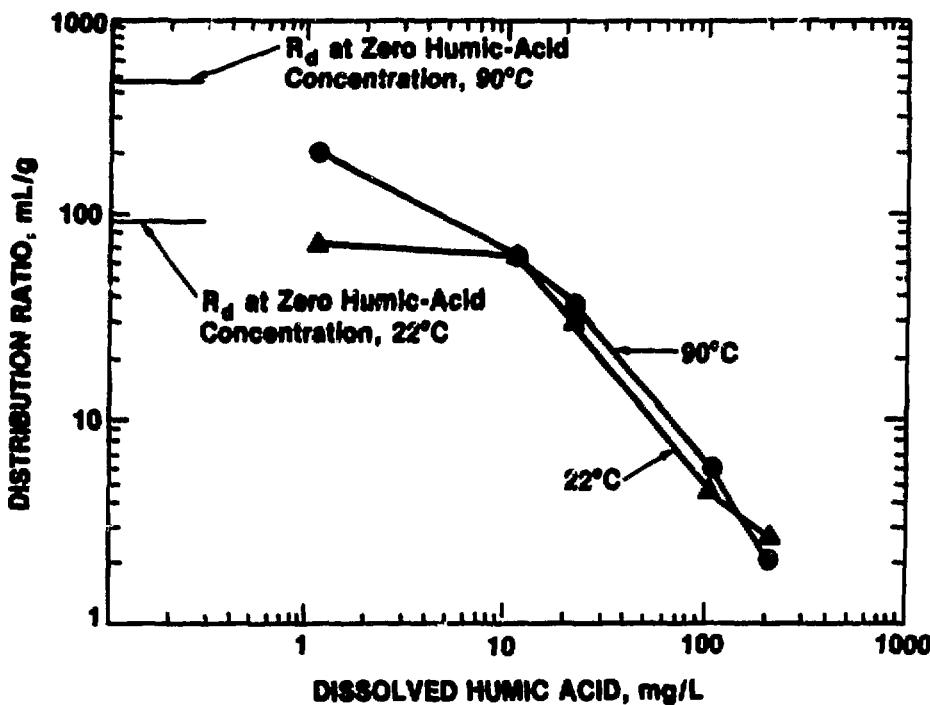
Fig. 24. Distribution Ratios (R_d) for Americium between
Synthetic Groundwater and Granulated Pomona
Basalt Reacted Seven Days in the Presence of
Various Concentrations of Humic Acid. Initial
pH of solutions adjusted to 9.2.
[BOGGS-1984A].

carbon. This figure suggests that solubilization of Am can be measurably
increased by as little as 1 ppm DOC above zero level. At higher DOC concen-
trations, solubilization increased essentially linearly with increasing HA
concentration within the range of 10 to 200 mg(C)/L. Similar results were
obtained in experiments with both Am and Np in FA and HA solutions in which
pH ranged from 9.9 (0 mg/L DOC) to 8.8 (200 mg/L DOC). Figure 25 shows the
results of experiments with Np and HA. In all experiments, a strong trend
of decreased sorption (increased complexation) of the radionuclide with
increasing concentration of HA or FA was established.
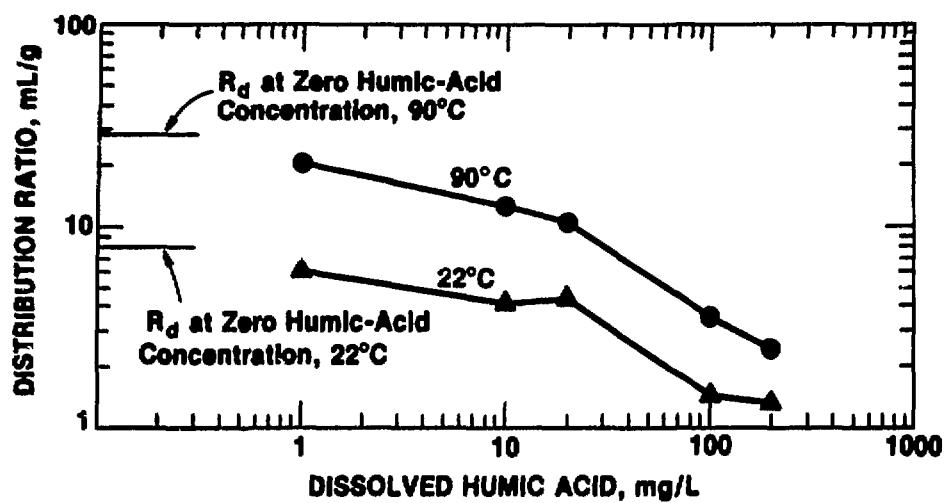
Fig. 25. Distribution Ratios (R_d) for Neptunium between
Synthetic Groundwater and Granulated Pomona
Basalt Reacted Seven Days in the Presence of
Various Concentrations of Humic Acid.
[BOGGS-1984A].

V. SUMMARY AND CONCLUSIONS

A. **Distribution and Characterization of Dissolved Humic Substances in Natural Waters**

Natural waters contain dissolved organic carbon (DOC) in concentrations ranging from as little as 0.1 mg/L in ocean water and unpolluted fresh water to more than 100 mg/L in some organic-rich lakes and swamps. A weighted world average of 5.75 mg/L DOC for streams has been reported. Groundwaters contain up to about 20 mg/L DOC; however, the average range of DOC values reported in one study of 100 groundwaters is 1.2 mg/L.

Dissolved organic substances encompass a wide range of compounds including humic substances, amino acids, fatty acids, phenols, sterols, carbohydrates, and porphyrins. Humic substances make up about 40 to 80% of the dissolved organics in surface waters. Groundwaters appear to contain somewhat less humic organic matter.

Humic compounds are poorly characterized, chemically and structurally complex, polyelectrolyte-like materials that range in molecular weight from a few hundred to several thousands. They can be subdivided into three fractions based on their solubility in acid and alkaline solutions: (1) humic acid (HA), which is soluble only in alkaline solutions; (2) fulvic acid (FA), which is soluble in both acid and base; and (3) humin, which is insoluble in both acid and base. Humic substances are composed predominantly of carbon, oxygen, hydrogen, and nitrogen, with small amounts of sulfur. These elements combine to form functional groups (structurally distinct arrangements of atoms) that play a dominant role in chemical reactions involving humic substances. The principal functional groups in humic materials are carboxyls, carbonyls, esters, ethers, alcoholic hydroxyls, phenolic hydroxyls, ketones, methoxyls, and quinones.

The dissolved humic substances (HA and FA) in surface waters are derived from soils where they originate by plant alteration, chemical polymerization, or microbial synthesis. The humic substances in groundwaters also appear to be derived mainly by leaching of humic materials from soils; however, some groundwater HA and FA may originate by leaching of fine particulate organic matter that was deposited concurrently with the sediments that make up the aquifer rock.

Humic substances can be studied and characterized by a wide variety of analytical methods. Nondestructive analytical methods include UV and infrared spectrometry, nuclear magnetic resonance spectrometry, X-ray analysis, electron microscopy, viscosity measurements, surface tension measurements, molecular weight measurements (particularly by gel filtration techniques), and electro-metric titration. Destructive analytical techniques include various types of degradation (oxidative, reductive, hydrolytic, thermal, radiochemical, biolog-ical) as well as pyrolysis-gas chromatography. Degradative methods particularly are used to study the structure of HA and FA.

Interaction of Humic Substances with Metals

Humic substances can combine chemically with metal ions to form metal-
mate complexes. A metal complex is a chemical species that contains a metal
om bonded to a greater number of ions or molecules than would be expected
on simple valency considerations. Chelates are a special type of metal-
ganic complex in which the ligands (the ions or molecules bonded or coor-
nated with the metal ion) are bonded to the metal ion through two or more
fferent ligand atoms. The ligands thereby form part of heterocyclic rings
which the metal is one of the members.

The tendency of metals to form complexes with humic substances in aqueous
lutions can be measured by an empirically determined conditional stability
nstant (K') that is derived from the relationship

$$K' = \frac{[ML]}{[M] \, [L]} \tag{38}$$

ere ML refers to bound metal (complexed with organic ligands), M refers to
ne metal ions, L refers to organic ligands, and the brackets indicate con-
ntration. Conditional stability constants vary with the ionic strength of
a aqueous solution and, thus, differ from true thermodynamic stability con-
ants, which are based on the activities of metals and ligands and are inde-
ndent of ionic strength. Thermodynamic stability constants for metal-humic
mplexes commonly cannot be calculated owing to the fact that HA and FA do
: have fixed chemical compositions, and activity-coefficient data for humic
ustances are generally inadequate or unknown. Larger values of conditional
ability constants indicate a greater tendency toward complex formation and
ater stability of the complex or chelate.

In addition to forming soluble complexes with metals, humic materials can
so interact with metal ions to form colloids composed of water-insoluble
tal humates. Humic substances have negative charges; therefore, they can
readily coagulated by electrolytes to form colloids. In general, trivalent
ns are more effective in coagulating humic substances than divalent ions,
I divalent ions are more effective than monovalent ions. The chemistry of
loids is still poorly understood, however, and the overall importance of
tal-humic colloid formation in natural waters remains to be established.

Several factors have been demonstrated to affect the formation and
bility of metal-humic complexes in natural waters. These factors include
: concentrations and types of metal ions and humic substances as well as
vironmental variables such as pH and ionic strength. The effect of each
these parameters is briefly summarized below.

1. Type of Metal Ion

Some metal ions are weakly bound to humic substances, whereas others
: much more firmly bound. It is difficult to make generalizations about the
perties of metal ions that affect bond strength, although it has been pro-
ied that bond strength varies inversely with the ionic radius and the second
lization potential of the metals. One empirical study determined that the

common metals can be broken down into three groups according to the relative strengths of their bonds with humic substances: (1) strong: Fe^{3+}, Hg^{2+}; (2) intermediate: Cu^{2+}, Pb^{2+}, Al^{3+}; and (3) weak: Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}.

2. Type of Organic Matter

Data on the relative binding strengths of HA versus FA are few, although many investigators suggest that the latter binds metals more strongly than the former. By contrast, one study of the binding of copper by HA and FA reported the opposite trend. The binding capacities of HA and FA with copper were found to vary among HA and FA from different sources; however, in all cases where the binding capacities of HA and FA from the same general environment were compared, HA was a stronger binder of Cu^{2+} than FA.

3. Metal and HA-FA Concentrations

The effects of changes in metal or HA-FA concentration are commonly expressed as a ratio; i.e., [M]/[HA] or [M]/[FA]. Most studies have demonstrated that decreases in these ratios cause an increase in the stability of metal-organic complexes. That is, an increase in the concentration of HA or FA or a decrease in metal concentration causes an increase in the tendency to form metal-humic complexes and in the stabilities of these complexes.

4. pH

With few exceptions, studies of pH have found a general increase in stability of metal-humic complexes with increasing pH. Increasing complexation with increasing pH is apparently the result of decreasing competition between metal ions and H^+ ions for binding sites on the negatively charged organic substances.

5. Ionic Strength

Increase in ionic strength of aqueous solutions causes a decrease in the stability of metal-humic complexes. Metals that form strong complexes with humic substances appear to be affected more strongly by changes in ionic strength than those that form weaker complexes. That is, the stability of strongly bonded metal-humic complexes decreases more rapidly with increasing ionic strength than that of weakly bonded complexes. This trend of decreasing stability with increasing ionic strength reflects the effects of increased competition by other cations in solution for binding sites on the humic materials.

C. Complexing of Radionuclides by Organic Substances

Humic substances also form soluble and insoluble complexes with radionuclides, including the actinide elements. Radionuclides may interact with humic materials in the soil environment or in surface waters or groundwaters. In the soil environment, radionuclides can form either mobile soluble complexes, or insoluble complexes that may remain attached to soil particulates such as clay minerals. They may also form "radiocolloids" that precipitate and remove radionuclides from solution. The relative importance of the

processes that form soluble versus insoluble complexes, which have opposing effects on radionuclide mobility, remains to be established. Studies of some radionuclides have shown a tendency for the radionuclides to become fixed in the soils by adsorption to humic substances that are firmly bound to clay minerals or other particulates in the soils. Studies of other radionuclides show increased mobility of the radionuclides owing to complexing with soluble HA or FA.

Many radionuclides form strong, stable, soluble complexes with dissolved HA and FA in surface waters and groundwaters. Under some conditions, stable insoluble complexes (colloids) may also form. Stable soluble complexes appear more likely to form than colloids, given the low concentrations of radionuclides present in most natural waters; however, the conditions that favor formation of colloids over soluble complexes are poorly understood. A few available data suggest that colloid formation is favored by increasing radionuclide concentration and low pH values. Also, HA appears to cause flocculation and colloid formation more readily than FA. The tendency toward colloid formation also appears to vary with the type of radionuclide. For example, some preliminary data suggest that, at low pH, Th and Am have a greater tendency to cause flocculation of HA and FA than Pu, Np, and U.

Numerous studies have now established that the formation of soluble radionuclide-humic complexes is generally favored by increased concentrations of HA and FA. The oxidation state of actinide elements and the pH also have a pronounced effect on complex formation. Other factors that affect the stability of radionuclide-organic complexes include radionuclide concentration, ionic strength, and temperature. The principal effects of these variables are summarized below.

1. Oxidation State

The oxidation state of the actinide elements, many of which exist in multiple oxidation states, appears to be one of the most important controls on their chemical behavior. The stable oxidation state of the environment is governed by the presence of oxidizing and reducing agents and complexing ligands. Organic substances act not only as complexants but also as reducing agents; thus, radionuclides are likely to exist in their lower oxidation states in the presence of large concentrations of dissolved organic substances. In general, the actinides appear to be more soluble in their higher oxidation states than in their reduced forms. Actinide elements that have the same oxidation state tend to behave similarly chemically; e.g., the behavior of Pu(III) is similar to that of Am(III). The presence of dissolved humic substances in aqueous systems has two opposing tendencies on the mobility of the actinide elements. On the one hand, humic substances bring about the reduction of actinides such as Pu(V) to Pu(IV), causing a decrease in solubility and mobility; however, competitive chelation caused by the increased tendency to formation of soluble complexes in the presence of HA and FA acts in the opposite direction to increase mobility.

2. pH

The complexing of actinides with HA and FA is strongly dependent upon pH, because both the hydrolysis of the nuclides and the dissociation of the acids are pH dependent. Also, pH affects the oxidation states of the

actinides; i.e., in general, lower oxidation states are favored by acidic conditions. Most studies that have examined the effects of pH on radionuclide-organic complexing have found a general trend of increasing complex formation (solubilization of the radionuclide) with increasing pH, although the trend is not linear. In general, neutral to basic pH values favor complexation and solubilization over acidic pH values. This trend appears to be opposite to that found in most studies of radionuclide sorption onto rock materials that have been carried out in solutions free of humic substances. These adsorption studies typically show that radionuclide adsorption onto rock materials increases (solubility decreases) as the pH increases, although this trend may not hold over the entire range of pH values. Thus, increasing pH appears to favor formation of soluble complexes of radionuclides in the presence of humic substances and decreased sorption onto solid phases, in contrast to increased sorption onto solid phases in the absence of humic substances.

3. Temperature

Studies of radionuclide sorption onto rock materials in solutions free of organic complexants show, in general, that increase in temperature favors increased sorption onto the rock (decreased solubilization of the nuclide), although the exact effect depends upon the radionuclide involved and the temperature range. That is, sorption may not increase through all temperature ranges for a particular radionuclide, and may not increase at all for some radionuclides. When dissolved humic substances are added to solutions at a given temperature, the general effect is to increase solubilization and decrease sorption. Preliminary data suggest that if temperature is then increased, a general trend of decreasing solubilization (increasing sorption) is observed, though the effects vary with different radionuclides and within different temperature ranges. Thus, increased sorption of radionuclides onto rock materials at higher temperatures occurs both in solutions containing organic complexants and in those free of such complexants, although the presence of organic substances decreases sorption in all temperature ranges and the effects of temperature on sorption appear to be less severe in solutions with high concentrations of organics than in those with lower concentrations. It is difficult to conclude from these sorption studies whether increasing temperature does or does not increase the stability of radionuclide-organic complexes. Experimental results need to be recast in terms of conditional stability constants that are calculated for experimental runs made over a range of temperatures and where all other solution and environmental parameters are held constant.

4. Ionic Strength

Only a few studies have examined the effects of ionic strength on radionuclide-organic complexing. One well-documented study of Eu binding by FA demonstrated a significant decrease in binding of Eu with increasing ionic strength of NaCl solutions within the range of 0.05 to 0.30M. Presumably, ionic strength affects other radionuclides in a similar manner. Thus, preliminary studies suggest that the stability of radionuclide-organic complexes, like that of trace metal-organic complexes, decreases in the presence of increasing concentrations of competing cations.

Inorganic ligands such as HCO_3^- and SO_4^{2-} may also affect radionuclide-organic complexing by competing with organic ligands for available nuclide ions. In the alkaline groundwater environment, carbonate is the most likely inorganic ligand to interact with radionuclides. Some available data suggest that the relative bond strength of radionuclide-humic complexes and radionuclide-CO_3^{2-} complexes varies with the source of the humic material and the pH. In one study, it was found that Eu can be complexed more strongly at pH 8 by as little as 2 ppm FA than by CO_3^{2-}, when the HCO_3^- concentration does not exceed 250 ppm. In another study of Pu complexing in seawater, the complexing of Pu with 20 mg/L DOC appeared actually to be enhanced by the presence of carbonate ion. On the other hand, a study of radionuclide-organic complexing in a high-alkalinity lake demonstrated that Pu complexing with the DOC of the lake water was little affected by high alkalinity, but that the complexing behavior of U appeared to be controlled by alkalinity rather than DOC concentration. Obviously, the effects on radionuclide-organic complexes caused by the presence of inorganic ligands depend upon the type of radionuclide and the pH—and probably other factors as well. Too few data are available to draw a more definite conclusion.

5. Radionuclide Concentration

A general trend of decreasing complex stability with increasing radionuclide concentration has been observed in most studies of radionuclide-organic complexing. This is the same trend reported in most studies of trace metal-organic complexing. This tendency indicates that if HA or FA concentration in a solution is held constant, further addition of radionuclide to the solution will decrease the capacity of the solution to form soluble radionuclide-organic complexes.

6. Humic and Fulvic Acid Concentration

It has now been clearly established that HA and FA have a solubilizing effect on most radionuclides as a result of forming stable, soluble complexes with the radionuclides. Concentrations of dissolved humic materials as low as 1 mg(C)/L have been shown to have a measurable effect on solubilization. Several studies have established that complexation increases with increasing concentration of HA or FA, in some cases almost linearly. Most experimental studies of radionuclide complexing by humic materials have been carried out using purified HA or FA extracted from soils. The process of extraction and purification removes most to the naturally complexed metal ions (such as Fe) from these humic materials, making them much more receptive to complexing with radionuclides than the indigenous humic substances dissolved in surface waters and groundwaters. There is a need now to carry out more definitive studies on radionuclide complexing by these indigenous humic materials, particularly the humic substances in deep groundwaters that are likely to be subjected to the greatest impact from radionuclides escaping from deep radioactive-waste repositories. Succeeding studies will have to examine the effects on complexing of small changes in the concentration of indigenous DOC within the limited range of about 1 to 10 mg/L, which are likely to be encountered in deep groundwaters.

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